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Variational methods, bounds and size effects for two-phase composites with coupled heat and mass transport processes at the two-phase interface

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Abstract

New variational principles are developed for the effective heat conductivity tensor of anisotropic two-phase composites in the presence of coupled mass and heat transport processes at the two-phase interface. We focus on physical situations where an imposed temperature gradient causes impurities or lattice defects to concentrate on the two-phase interface and diffuse along it. This is accompanied by the release and absorption of heat as the impurities, respectively, enter or leave the interface. We investigate the effect of the inclusion geometry on the overall thermal conductivity. For randomly distributed inclusions new size effects are given in terms of the inclusion size distribution and nearest neighbor distribution function for the included phase.

Keywords: A. Diffusion; Bulk; B. Ceramic material; C. Variational calculus

1. Introduction

We consider the overall thermal conductivity of two-phase composites in the presence of coupled mass and heat transport processes at the two-phase interface. We focus on physical situations where an imposed temperature gradient causes impurities or lattice defects to concentrate at the two-phase interface and diffuse along it. This process is accompanied by the release and absorption of heat as the impurities enter or leave the interface. The heat release and absorption, due to the segregation–surface diffusion of impurities, provides a heat flux in addition to the heat flux due to thermal conduction. This type of process was proposed in the work of Litovsky and Klimovich (1978), to explain the anomalous decrease in the effective thermal conductivity of porous ceramics at low pressures and temperatures around 1000°C.

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The physico-mathematical model for heat transfer considered in this paper is the one introduced by Gambaryan et al. (1993). Their model is given in the context of porous ceramics, but it applies to two-phase particle reinforced composites as well. To fix ideas and to make connection with earlier work, the analysis and results presented here are given in the context of porous ceramic materials. However, our results apply immediately to two-phase particle reinforced materials in the presence of a segregation–surface diffusion process on the two-phase interface.

We investigate the effect of the micro-geometry on the overall thermal conductivity in the presence of segregation–surface diffusion. Most often the composite geometry can only be characterized statistically. For randomly distributed inclusions new size effects are given in terms of the inclusion volume fraction, size distribution and nearest neighbor distribution function for the included phase: see Sections 5–7. These results provide guidelines for the design of porous ceramics and particle reinforced composites in the presence of coupled heat and mass transport at the two-phase interface.

We consider a porous ceramic material where the pore phase is filled with a gas of isotropic thermal conductivity σ_p. Away from the pore boundary the ceramic matrix has isotropic thermal conductivity σ_m. Normally, the thermal conductivity σ_p of the gas is less than the matrix σ_m and in this article we suppose

$$\sigma_m > \sigma_p.$$

The diffusivity associated with the diffusion of impurities in the ceramic matrix is denoted by D. The temperature field in the porous ceramic is continuous across the pore–matrix interface and is denoted by T. The volumetric concentration of impurities inside the matrix is C. On the matrix–pore interface the surface concentration of impurities C_s is assumed to be a decreasing function of temperature and increasing with the local bulk concentration C. The explicit formula for C_s, in terms of the variables T and C, depends upon the model used to describe the equilibrium surface concentration at the interface, see Kingrey (1974) and Kingrey et al. (1976). For now we linearize and write

$$C_s = C_{s0} + \alpha_T(T - T_0) + \alpha_C(C - C_0), \tag{1.1}$$

where C_{s0} is the equilibrium surface concentration and the coefficients

$$\alpha_T = \left(\frac{\partial C_s}{\partial T}\right)\Big|_{C_0,T_0}, \quad \alpha_C = \left(\frac{\partial C_s}{\partial C}\right)\Big|_{C_0,T_0} \tag{1.2}$$

are evaluated at their equilibrium values C_0, T_0. The coefficient α_T is negative since C_s decreases with temperature.

The surface diffusivity on the pore–matrix interface has dimensions of length $\times$ diffusivity and is denoted by α_s. The temperature field inside and outside the pores satisfies Fourier's law of thermal conduction:

$$\Delta T = 0. \tag{1.3}$$

The volumetric concentration of impurities in the ceramic matrix satisfies

$$\Delta C = 0. \tag{1.4}$$

It is assumed that the mass transfer occurs on the pore surface and that the impurities do not penetrate into the gas within the pore. Conservation of mass for impurities on the pore surface is given by

$$\nabla_s \cdot (\alpha_s \nabla_s C_s) = -D\mathbf{n} \cdot \nabla C. \tag{1.5}$$

Here $\mathbf{n}$ is the unit normal vector directed into the matrix phase and ∇_s is the surface gradient. The heat and mass fluxes are coupled on the pore surface through the relation

$$\sigma_m \mathbf{n} \cdot (\nabla T)|_{\text{matrix}} - \sigma_p \mathbf{n} \cdot (\nabla T)|_{\text{pore}} = -QD\mathbf{n} \cdot \nabla C. \tag{1.6}$$

Here Q is the specific heat release of the segregation process. Equation (1.6) accounts for the release and absorption of heat as the impurities enter or leave the interface. Equations (1.1)–(1.6) constitute the physico-mathematical model for heat and mass transport in two-phase (or multi-phase) materials in the presence of surface segregation–diffusion processes.

We consider a cube Ω of side length L containing the porous ceramic material. No assumptions on the distribution of pores within the interior of the cube are made. One can think of the cube as representing a (possibly very complicated) period cell for a porous ceramic. Prescribing the average temperature gradient $\mathbf{E}$ across the cube, the net heat flux $\mathbf{j}$ is measured and the effective conductivity tensor σ^e provides the linear relation between the average temperature gradient and net heat flux passing through the porous ceramic:

$$\mathbf{j} = \sigma^e \mathbf{E}. \tag{1.7}$$

Our approach to characterizing the effective conductivity is variational and is not tied to a particular composite geometry, approximate formula, or dilute approximation. New variational principles are introduced from which new bounds on the effective conductivity are obtained through simple choices of trial fields (see Sections 2, 3, 5 and 6). The attractive feature is that any observation deduced from the bounds is not tied to a particular geometry or approximate formula and will apply to a large class of statistically defined composite systems.

We introduce Dirichlet and Thompson-like variational principles describing the effective thermal conductivity σ^e. From these we build two more variational principles that implicitly contain extra information on the composite geometry: see Theorems 3.1 and 3.2. The approach is motivated by the idea that variational principles containing extra geometric information provide tighter bounds than those obtainable from the Dirichlet or Thompson-like variational principles for any given class of trial fields. The variational principles introduced here incorporate geometric information through the solution operators of simpler comparison problems. These operators admit an explicit representation either in terms of gradients of simple layer potentials supported on the pore–matrix interface, projection operators on the space $L^2(\Omega)^3$, or are associated with simple Dirichlet or Neumann problems in each phase (see Section 3). New bounds and variational principles have been derived using this approach in the context of two-phase conductors separated by a highly conducting interface in

Lipton (1997). For two-phase composites with interfacial thermal barriers this approach has been used to derive new bounds and variational principles by Lipton and Vernescu (1996). Moreover, this approach has been successful in the context of two-phase elastic composites with imperfect bonding at the interface. See Lipton and Vernescu (1995).

Substitution of simple trial fields into the upper variational principle delivers a new upper bound on the effective conductivity that depends upon pore volume fraction, a surface energy tensor and a scale free matrix of parameters. The scale free matrix of parameters corresponds to the effective thermal conductivity σ^{∞} associated with the pore phase filled with a perfect heat conductor and a matrix phase of unity conductivity. The surface energy tensor is proportional to the surface energy tensor introduced by Chandrasekhar (1965) for the stability analysis of rotating liquid drops held together by surface tension, see Theorem 5.2. The lower variational principle, Theorem 3.2, delivers a lower bound in terms of the pore volume fraction, the harmonic mean of the surface to volume dissipation of the pore phase, the two point correlation function associated with the pore phase and a second scale free matrix of parameters, see Theorem 6.5. Here the surface to volume dissipation of a pore, denoted by β, provides an estimate of the thermal energy dissipated inside a particle for a given thermal energy dissipation on its surface, see eqn (6.17). For a sphere of radius a, $\beta = 2/a$. The surface to volume dissipation was introduced in Lipton (1998) to describe new size effects for particle reinforced conductors with a highly conducting interface. The scale free matrix of parameters corresponds to the effective thermal conductivity σ^{0} associated with the pore phase filled with a perfect insulator and a matrix phase of unit conductivity.

When the composite geometry is statistically isotropic the bounds simplify. To fix ideas we consider the pore geometry to be given by a suspension of spheres of N different radii, $a_1, a_2, \ldots, a_N$. For a prescribed pore volume fraction θ_{p} we suppose that the volume fraction occupied by pores of radius a_i is given by the pore size distribution function $V(a_i)$ where $\Sigma_{i=1}^{N} \cdot V(a_i) = \theta_{\mathrm{p}}$. We write the mean of the radii as

$$\langle a \rangle = \theta_{\mathrm{p}}^{-1} \sum_{i=1}^{N} a_i V(a_i) \tag{1.8}$$

and the mean of the reciprocal radii is given by

$$\langle a^{-1} \rangle = \theta_{\mathrm{p}}^{-1} \sum_{i=1}^{N} a_i^{-1} V(a_i). \tag{1.9}$$

The upper bound on the effective conductivity is given in terms of the dimensionless constants

$$A_{\mathrm{T}} = \frac{(-\alpha_{\mathrm{T}})\alpha_{\mathrm{s}} Q}{\sigma_{\mathrm{m}} - \sigma_{\mathrm{p}}} \langle a^{-1} \rangle, \quad A_{\mathrm{C}} = \frac{\alpha_{\mathrm{C}} \alpha_{\mathrm{s}}}{D} \langle a^{-1} \rangle \left(\frac{\sigma^{\infty} - 1}{\theta_{\mathrm{p}}} - 1 \right)^{-1}. \tag{1.10}$$

The factor $\{[(\sigma^{\infty} - 1)/\theta_{\mathrm{p}}] - 1\}^{-1}$ is positive; this follows from the harmonic mean lower

bound $\sigma^{\infty} \geqslant (1-\theta_p)^{-1}$ and the estimate $(1-\theta_p)^{-1} > 1+\theta_p$. We introduce the variable Z defined by

$$Z = (\sigma_m - \sigma_p)\left(\frac{2A_T}{1-2A_C} - 1\right). \tag{1.11}$$

The upper bound is given by:

Theorem 1.1. Upper bound on effective thermal conductivity for polydisperse suspensions of spheres.

$$\sigma^e \leqslant \frac{\sigma_m(\theta_p Z + \sigma_m(1-(\sigma^{\infty})^{-1}))}{\theta_p Z(\sigma^{\infty})^{-1} + \sigma_m(1-(\sigma^{\infty})^{-1})}. \tag{1.12}$$

The lower bound is given in terms of the dimensionless constants

$$\tilde{A}_T = \frac{(-\alpha_T)\alpha_s Q}{\sigma_m - \sigma_p}\langle a\rangle^{-1}, \quad \tilde{A}_C = \frac{\alpha_C \alpha_s}{D}\langle a\rangle^{-1}\left(\frac{1-\sigma^0}{\theta_p} - 1\right). \tag{1.13}$$

Positivity of the factor $\{[(1-\sigma^0)/\theta_p]-1\}$ follows from the arithmetic mean upper bound $1-\theta_p \geqslant \sigma^0$. Introducing the variable t defined by

$$t = \theta_p(\sigma_m - \sigma_p)^{-1}\left(\frac{1+2\tilde{A}_C}{2\tilde{A}_T}\right), \tag{1.14}$$

the lower bound is given by:

Theorem 1.2. Lower bound on effective thermal conductivity for polydisperse suspensions of spheres.

$$\sigma^e \geqslant \sigma_p + \frac{(1-\theta_p)t + \dfrac{\theta_p^2}{\sigma_m - \sigma_p} + \dfrac{\theta_p}{3\sigma_p}}{\left(\dfrac{\theta_p}{3\sigma_p} + \dfrac{1}{\sigma_m - \sigma_p}\right)t + \dfrac{\theta_p(1-\theta_p)}{3\sigma_p(\sigma_m - \sigma_p)}}. \tag{1.15}$$

The upper and lower bounds are monotonic in the parameters Z and t, respectively. Several conclusions follow from the monotonicity and are given in Sections 5 and 6. The principal result is given in the following Theorem.

Theorem 1.3. Energy dissipation inequality.

For any value of the pore volume fraction θ_p we have the following:

If

$$\frac{2A_T}{1+2A_C} \leqslant 1, \tag{1.16}$$

them

$$\sigma^{e} \leqslant \sigma_{m}. \tag{1.17}$$

On the other hand, when

$$\frac{2\tilde{A}_{T}}{1+2\tilde{A}_{C}} \geqslant 1, \tag{1.18}$$

then

$$\sigma^{e} \geqslant \sigma_{m}. \tag{1.19}$$

It is emphasized that this theorem holds for all statistically isotropic porous ceramics and that no approximations have been made. In physical terms, the parameters A_T and $\tilde{A}_T$ characterize the relative enhancement of the heat flux across a pore due to the segregation–diffusion process, while A_C and $\tilde{A}_C$ are measures of the mass transfer of impurities from the matrix to the pore surface relative to the flux of impurities in the neighborhood surrounding the pore. The physical interpretation for these parameters and their relation to the parameters derived in Gambaryan et al. (1993) is discussed in Section 7.

For fixed values of the parameters σ_m, σ_p, D, α_s, α_T, α_C and Q, Theorem 1.3 implies a particle size effect.

Theorem 1.4. Pore size effect.

For any value of the pore volume fraction θ_p we have the following:

If

$$\langle a^{-1}\rangle^{-1} \geqslant \frac{2Q\alpha_s(-\alpha_T)}{\sigma_m-\sigma_p} - 2\alpha_s\left(\frac{\alpha_C}{D}\right)\left(\frac{\sigma^{\infty}-1}{\theta_p}-1\right)^{-1}, \tag{1.20}$$

then

$$\sigma^{e} \leqslant \sigma_{m}. \tag{1.21}$$

On the other hand, when

$$\langle a\rangle \leqslant \frac{2Q\alpha_s(-\alpha_T)}{\sigma_m-\sigma_p} - 2\alpha_s\left(\frac{\alpha_C}{D}\right)\left(\frac{1-\sigma^{0}}{\theta_p}-1\right), \tag{1.22}$$

then

$$\sigma^{e} \geqslant \sigma_{m}. \tag{1.23}$$

For a sufficiently large average pore radius, Theorem 1.4 shows that the effective conductivity drops below the thermal conductivity of the matrix, while if the average pore radius is sufficiently small the effective conductivity is greater than that of the matrix phase. When the ratio α_C/D vanishes the average pore size at which the effective conductivity changes from being lower than the matrix conductivity to being greater than that of the matrix is given by:

$$\frac{2Q\alpha_s(-\alpha_T)}{\sigma_m-\sigma_p}, \tag{1.24}$$

and Theorem 1.4 recovers the size effect theorem for composites with a highly conducting interface given in Lipton (1997a). When $\alpha_C = 0$ and all pores have the same radius, Theorem 1.4 predicts the existence of a critical pore radius $R = [2Q\alpha_s(-\alpha_T)/(\sigma_m-\sigma_p)]$ for which the effective conductivity equals that of the matrix material. It is evident from Theorem 1.4, that nonzero values of the ratio α_C/D lower the average pore size at which the transition occurs. This effect is seen most clearly for dilute suspensions of pores. For a dilute suspension of pores all having the same radius a we expand the effective conductivities σ^∞ and σ^0 in their dilute expansions given by:

$$\sigma^\infty = 1+3\theta_p+O(\theta_p^2) \quad \text{and} \quad \sigma^0 = 1-\tfrac{3}{2}\theta_p+O(\theta_p^2). \tag{1.25}$$

Substitution of the expansions into the formulas for A_C, $\tilde{A}_C$, A_T and $\tilde{A}_T$ gives:

Theorem 1.5. Pore size effect for dilute pore concentrations.

When $\theta_p \ll 1$ we have:

If

$$a \geqslant \frac{2Q\alpha_s(-\alpha_T)}{\sigma_m-\sigma_p} - \frac{\alpha_s\alpha_C}{D}(1+O(\theta_p)), \tag{1.26}$$

then

$$\sigma^e \leqslant \sigma_m. \tag{1.27}$$

On the other hand, when

$$a \leqslant \frac{2Q\alpha_s(-\alpha_T)}{\sigma_m-\sigma_p} - \frac{\alpha_s\alpha_C}{D}(1+O(\theta_p)), \tag{1.28}$$

then

$$\sigma^e \geqslant \sigma_m. \tag{1.29}$$

Theorems 1.1–1.4 are generalized to statistically isotropic composites containing pores of arbitrary shape in Theorems 5.3, 5.4, 6.6 and 6.7. In this general context the bounds are given in terms of the specific interfacial surface area and the harmonic mean of the surface to volume dissipation of the pore phase.

The effective conductivities σ^∞ and σ^0 appearing in the bounds (1.12) and (1.15), are bounded by expressions containing statistical information on the pore geometry. For monodisperse suspensions of spherical pores we use the security sphere bounds of Torquato and Rubinstein (1991). These provide upper and lower bounds on σ^∞ and σ^0 in terms of the nearest neighbor distribution function. The nearest neighbor distribution function for spherical pores can be calculated using the methods developed in Torquato et al. (1990). For polydisperse suspensions of pores we use the

bounds derived by Bruno (1991). These bounds are given in terms of the parameter 'q'. Here, q is defined to be the minimum, over all pores in the suspension, of the ratio of pore radius to distance from the pore center to its nearest neighbor in the suspension. The bounds (1.12) and (1.15) are monotone in σ^{∞} and σ^{0}. Thus, substitution of bounds on σ^{∞} and σ^{0} into (1.12) and (1.15) delivers bounds on σ^{e} in terms of the nearest neighbor distribution function or q. These observations are applied in Theorems 5.5 and 5.6 in Section 5 and Theorems 6.8 and 6.9 in Section 6. These bounds deliver new pore size effects for the effective thermal transport properties and are in terms of partial statistical information on the pore configuration. These bounds are plotted for random, monodisperse suspensions of spherical pores in Section 7.

2. New Dirichlet and Thompson variational principles

For a prescribed average temperature gradient $\mathbf{E}$, the temperature field T is decomposed into a periodic fluctuation $\tilde{\varphi}$ and a prescribed linear part $\mathbf{E}\cdot\mathbf{x}$, i.e., $T=\tilde{\varphi}+\mathbf{E}\cdot\mathbf{x}$. The average temperature gradient seen by an outside observer is:

$$\mathbf{E}=|\Omega|^{-1}\int_{\partial\Omega} T\mathbf{n}\,\mathrm{d}s. \tag{2.1}$$

Here $\partial\Omega$ is the boundary of the cube of side length L, $\mathbf{n}$ is the unit outer normal to the boundary and $|\Omega|=L^3$ is the volume of the cube. Denoting the local conductivity in the porous ceramic by $\sigma(\mathbf{x})$, the overall heat flux $\mathbf{j}$ measured by an outside observer is given by

$$\mathbf{j}=|\Omega|^{-1}\int_{\partial\Omega}(\tilde{\mathbf{j}}\cdot\mathbf{n})\mathbf{x}\,\mathrm{d}s, \tag{2.2}$$

where $\tilde{\mathbf{j}}=\sigma(\mathbf{x})\nabla T$. The associated effective conductivity of the sample is defined by (1.7). Integration by parts, application of (1.1)–(1.6) and the natural boundary condition for the heat and concentration flux yields:

$$\sigma^{e}\mathbf{E}\cdot\mathbf{E}=|\Omega|^{-1}W(\tilde{\varphi},C). \tag{2.3}$$

Here $W(\tilde{\varphi},C)$ is given by

$$W(\tilde{\varphi},C)=\int_{\Omega}\sigma(\mathbf{x})|\nabla\tilde{\varphi}+\mathbf{E}|^2\,\mathrm{d}x + \frac{\alpha_C}{(-\alpha_T)}\int_{\Omega_m} QD|\nabla C|^2\,\mathrm{d}x+\frac{1}{(-\alpha_T)}\int_{\Gamma}\alpha_s Q|\nabla_s C_s(\tilde{\varphi},C)|^2\,\mathrm{d}s, \tag{2.4}$$

where Ω_m is the part of the sample occupied by the matrix phase, Γ is the union of all pore boundaries and the surface concentration on the pore boundary is given by $C_s(\tilde{\varphi},C)=\alpha_T(\tilde{\varphi}+\mathbf{E}\cdot\mathbf{x}-T_0)+\alpha_C(C-C_0)$. We introduce the space of trial fields U defined by:

$$U = \{(\varphi, \mathscr{C}) \text{ such that } \varphi \text{ is in } H^1(\Omega)_{\text{per}} \text{ and } \mathscr{C} \text{ is in } H^1(\Omega_{\text{m}})_{\text{per}}\}, \tag{2.5}$$

where $H^1(\Omega)_{\text{per}}$ comprises all periodic continuous square integrable fields with square integrable derivatives and $H^1(\Omega_{\text{m}})_{\text{per}}$ are all such fields restricted to the matrix phase. The Dirichlet-like variational principle for the effective conductivity is given by:

Theorem 2.1. Dirichlet-like variational principle.

$$\sigma^{\text{e}}\mathbf{E}\cdot\mathbf{E} = |\Omega|^{-1} \min_{(\varphi,\mathscr{C}) \text{ in } U} W(\varphi, \mathscr{C}). \tag{2.6}$$

Existence of the minimizer $(\tilde{\varphi}, C)$ for the variational principle follows easily from the direct method of the calculus of variations. Stationarity conditions show that the minimizer is precisely the temperature and concentration satisfying the equilibrium equations (1.1)–(1.6). The minimizer is easily seen to be unique up to a constant temperature and concentration.

We represent a jump in a quantity 'f' across the pore–matrix boundary by $[f] = f|_{\text{pore}} - f|_{\text{matrix}}$. The boundary of the ith pore is denoted by Γ_i and $\Gamma = \cup_i \Gamma_i$. The set of all points in Ω not on the pore–matrix interface is denoted by Ω/Γ. The space of functions that are square integrable and have square integrable tangential derivatives in the pore–matrix interface is denoted by $H^1(\Gamma)$. We consider porous ceramics for which the pores do not intersect the boundary of the domain Ω. We make this assumption for convenience only and to keep the exposition focused. (What follows applies to any periodic porous geometry.) We introduce the space of trial fields V given by

$$V = \tilde{\mathbf{p}} \quad \text{in } L^2(\Omega)^3,$$

where:

$$\operatorname{div} \tilde{\mathbf{p}} = 0 \quad \text{in } \Omega/\Gamma \tag{2.7}$$

$$\int_{\partial\Omega} (\tilde{\mathbf{p}}\cdot\mathbf{n})\mathbf{x}\, \mathrm{d}s = 0, \tag{2.8}$$

$$\int_{\Gamma_i} [\tilde{\mathbf{p}}\cdot\mathbf{n}]\, \mathrm{d}s = 0, \tag{2.9}$$

$$\tilde{\mathbf{p}} \quad \text{is periodic on } \partial\Omega. \tag{2.10}$$

Next we introduce the solution g in $H^1(\Gamma)$ of the Poisson equation on the interface given by

$$\alpha_{\text{T}}\Delta_{\text{s}} g = [\tilde{\mathbf{p}}\cdot\mathbf{n}] \quad \text{on } \Gamma_i. \tag{2.11}$$

Here Δ_{s} is the Laplace–Beltrami operator on the surface Γ_i and g is determined uniquely up to a constant for $\tilde{\mathbf{p}}$ satisfying the solvability condition (2.9). We also consider the periodic function w satisfying the Neumann problem

$$\Delta w = 0 \quad \text{on } \Omega_{\text{m}} \tag{2.12}$$

$$-\nabla w \cdot \mathbf{n} = \frac{\alpha_C}{\alpha_T}[\tilde{\mathbf{p}} \cdot \mathbf{n}] \quad \text{on } \Gamma_i. \tag{2.13}$$

The Thompson-like variational principle is given by:

Theorem 2.2. Thompson-like variational principle.

For any prescribed constant heat flux $\tilde{\mathbf{p}}$ in R^3:

$$(\sigma^e)^{-1}\tilde{\mathbf{p}} \cdot \tilde{\mathbf{p}} = |\Omega|^{-1} \min_{(\tilde{\mathbf{p}} \text{ in } V)} L(\tilde{\mathbf{p}}), \tag{2.14}$$

where

$$L(\tilde{\mathbf{p}}) = \int_\Omega (\sigma(\mathbf{x}))^{-1}|\tilde{\mathbf{p}} + \bar{\mathbf{p}}|^2 \, dx + \alpha^{-1} \int_\Gamma |\nabla_s g|^2 \, ds + (\overset{*}{D})^{-1} \int_{\Omega_m} |\nabla w|^2 \, dx, \tag{2.15}$$

$$\overset{*}{D} = \frac{\alpha_C}{(-\alpha_T)} QD \quad \text{and} \quad \alpha = \frac{1}{(-\alpha_T)} \alpha_s Q. \tag{2.16}$$

Proof: We introduce the space of all square integrable periodic vector fields on Ω and denote it by $L^2(\Omega)^3_{\text{per}}$. The space of periodic square integrable vector fields defined on the matrix phase is denoted by $L^2(\Omega_m)^3_{\text{per}}$. The space of all square integrable vector fields restricted to the pore–matrix interface is denoted by $L^2(\Gamma)^3$. Starting with the Dirichlet-like variational principle we take the convex dual of each term in the functional $W(\varphi, \mathscr{C})$ to obtain

$$\sigma^e \mathbf{E} \cdot \mathbf{E} = \min_{(\varphi,\mathscr{C})} \max_{\mathbf{p} \in L^2(\Omega)^3_{\text{per}}} \max_{\mathbf{f} \in L^2(\Omega_m)^3_{\text{per}}} \max_{\mathbf{v} \in L^2(\Gamma)^3} |\Omega|^{-1} H(\varphi, \mathscr{C}, \mathbf{p}, \mathbf{f}, \mathbf{v}), \tag{2.17}$$

where

$$H(\varphi, \mathscr{C}, \mathbf{p}, \mathbf{f}, \mathbf{v}) = 2\int_\Omega \mathbf{p} \cdot (\nabla\varphi + \mathbf{E}) \, dx - \int_\Omega (\sigma(\mathbf{x}))^{-1}\mathbf{p} \cdot \mathbf{p} \, dx$$
$$+ 2\int_{\Omega_m} \mathbf{f} \cdot \nabla\mathscr{C} \, dx - (\overset{*}{D})^{-1} \int_{\Omega_m} |\mathbf{f}|^2 \, dx + 2\int_\Gamma \mathbf{v} \cdot \nabla_s C_s(\varphi, \mathscr{C}) \, ds - \alpha^{-1} \int_\Gamma |\mathbf{v}|^2 \, ds, \tag{2.18}$$

and we recall that

$$C_s(\varphi, \mathscr{C}) = \alpha_T(\varphi + \mathbf{E} \cdot \mathbf{x} - T_0) + \alpha_C(\mathscr{C} - C_0). \tag{2.19}$$

Exchanging max and min implies that the trial fields $\mathbf{p}$, $\mathbf{f}$ and $\mathbf{v}$ must be chosen such that

$$\min_{(\varphi,\mathscr{C})} \left(2\int_\Omega \mathbf{p} \cdot \nabla\varphi \, dx + 2\int_{\Omega_m} \mathbf{f} \cdot \nabla\mathscr{C} \, dx + 2\int_\Gamma \mathbf{v} \cdot \nabla_s C_s(\varphi, \mathscr{C}) \, ds \right) > -\infty. \tag{2.20}$$

Integration by parts reveals that (2.20) is equivalent to the constraints, $\operatorname{div} \mathbf{p} = 0$, for all points not on the pore–matrix interface,

$$[\mathbf{p} \cdot \mathbf{n}] = \alpha_T(\nabla_s \cdot \mathbf{v} + (\mathbf{n} \cdot \mathbf{v})\mathscr{I}) \quad \text{on } \Gamma_i, \tag{2.21}$$

$$-\mathbf{f}\cdot\mathbf{n}|_{\text{matrix}} = \alpha_C(\nabla_s\cdot\mathbf{v} + (\mathbf{n}\cdot\mathbf{v})\mathscr{I}) \quad \text{on } \Gamma_i, \tag{2.22}$$

$$\int_{\Gamma_i}[\mathbf{p}\cdot\mathbf{n}]\,ds = 0, \quad \text{and} \quad \int_{\Gamma_i}\mathbf{f}\cdot\mathbf{n}|_{\text{matrix}}\,ds = 0. \tag{2.23}$$

Here the mean curvature at any point on the pore–matrix interface is written $\mathscr{I} = -\operatorname{div}\mathbf{n}$, and for any $\mathbf{v}$ in $L^2(\Gamma)^3$ the surface divergence $\nabla_s\cdot\mathbf{v}$ is defined in the distributional sense. Substitution of these identities into (2.18) together with the identity

$$\int_{\Omega/\Gamma}\operatorname{div}((\mathbf{E}\cdot\mathbf{x})\mathbf{p})\,dx - \int_{\partial\Omega}(\mathbf{E}\cdot\mathbf{x})(\mathbf{p}\cdot\mathbf{n})\,ds = \int_{\Gamma}(\mathbf{E}\cdot\mathbf{x})[\mathbf{p}\cdot\mathbf{n}]\,ds \tag{2.24}$$

gives

$$\sigma^e\mathbf{E}\cdot\mathbf{E} \geqslant 2\int_{\partial\Omega}(\mathbf{E}\cdot\mathbf{x})(\mathbf{p}\cdot\mathbf{n})\,ds - \int_{\Omega}(\sigma(\mathbf{x}))^{-1}|\mathbf{p}|^2\,dx - (\overset{*}{D})^{-1}\int_{\Omega_m}|\mathbf{f}|^2\,dx - \alpha^{-1}\int_{\Gamma}|\mathbf{v}|^2\,ds, \tag{2.25}$$

for all choices of trials $\mathbf{p}$, $\mathbf{f}$, $\mathbf{v}$. We write

$$\bar{\mathbf{p}} = |\Omega|^{-1}\int_{\partial\Omega}(\mathbf{p}\cdot\mathbf{n})\mathbf{x}\,ds, \tag{2.26}$$

and $\tilde{\mathbf{p}} = \mathbf{p} - \bar{\mathbf{p}}$. Setting $\bar{\mathbf{p}} = \sigma^e\mathbf{E}$, or equivalently $\mathbf{E} = (\sigma^e)^{-1}\bar{\mathbf{p}}$, gives

$$(\sigma^e)^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} \leqslant |\Omega|^{-1}\left(\int_{\Omega}(\sigma(\mathbf{x}))^{-1}|\tilde{\mathbf{p}}+\bar{\mathbf{p}}|^2\,dx + \alpha^{-1}\int_{\Gamma}|\mathbf{v}|^2\,ds + (\overset{*}{D})^{-1}\int_{\Omega_m}|\mathbf{f}|^2\,dx\right). \tag{2.27}$$

For the choice $\bar{\mathbf{p}}+\tilde{\mathbf{p}} = \sigma(\mathbf{x})(\nabla\tilde{\varphi}+\mathbf{E})$, $\mathbf{E} = (\sigma^e)^{-1}\bar{\mathbf{p}}$, $\mathbf{v} = \alpha\nabla_s C_s(\tilde{\varphi}, C)$ and $\mathbf{f} = \overset{*}{D}\nabla C$ one satisfies the constraints implied by (2.20) and one obtains equality in (2.27). Last we note that the optimal choice of $\mathbf{v}$ and $\mathbf{f}$ are of the form $\nabla_s g$ and ∇w, respectively, where g satisfies (2.11) and w satisfies (2.12) and (2.13) and the theorem follows.

3. New variational principles

In this section we introduce new variational principles for the effective conductivity tensor. These principles encode geometric information on the pore structure through the solution operators of simpler conductivity problems. The variational principles provide the tools used to establish new pore size effects for the effective conductivity. Before introducing the first variational principle we introduce a homogeneous comparison material with conductivity $\gamma > \sigma_m$ and formulate three auxiliary conductivity

problems. For any constant vector $\mathbf{c}$ in R^3 we introduce the potential $\psi^{\mathbf{c}}$ in $H^1(\Omega)_{\text{per}}$ which solves

$$\psi^{\mathbf{c}} + \mathbf{c}\cdot\mathbf{x} = \text{const}_i^1 \quad \text{on } \Gamma_i, \tag{3.1}$$

$$\Delta\psi^{\mathbf{c}} = 0 \quad \text{in } \Omega/\Gamma \tag{3.2}$$

and

$$\int_{\Gamma_i} [\nabla\psi^{\mathbf{c}}\cdot\mathbf{n}]\,\mathrm{d}s = 0. \tag{3.3}$$

Inside each pore we note that the boundary conditions (3.1) together with (3.2) imply that $\psi^{\mathbf{c}}$ is linear inside each pore and is given by $\psi^{\mathbf{c}} = -\mathbf{c}\cdot\mathbf{x} + \text{const}_i^1$. We introduce the space $H(\text{div}, \Omega/\Gamma)$ of periodic, square integrable vector fields $\boldsymbol{\eta}$ for which $\text{div}\,\boldsymbol{\eta}$ is defined on Ω/Γ and is square integrable. We denote by $\mathscr{P}$ the space

$$\mathscr{P} = (\boldsymbol{\eta} \text{ in } H(\text{div}, \Omega/\Gamma), \text{ such that } \boldsymbol{\eta} \text{ is periodic on } \Omega). \tag{3.4}$$

For $\boldsymbol{\eta}$ in $\mathscr{P}$ and l in $H^1(\Gamma)$ we introduce the potentials ψ^l and $\psi^{\boldsymbol{\eta}}$ that are the solutions of

$$\psi^l = l + \text{const}_i^2 \quad \text{on } \Gamma_i, \tag{3.5}$$

$$\Delta\psi^l = 0 \quad \text{in } \Omega/\Gamma, \tag{3.6}$$

$$\int_{\Gamma_i} [\nabla\psi^l\cdot\mathbf{n}]\,\mathrm{d}s = 0, \tag{3.7}$$

and

$$\psi^{\boldsymbol{\eta}} = \text{const}_i^3 \quad \text{on } \Gamma_i, \tag{3.8}$$

$$\Delta\psi^{\boldsymbol{\eta}} = \text{div}\,\boldsymbol{\eta} \quad \text{in } \Omega/\Gamma, \tag{3.9}$$

and

$$\int_{\Gamma_i} [(\nabla\psi^{\boldsymbol{\eta}} - \boldsymbol{\eta})\cdot\mathbf{n}]\,\mathrm{d}s = 0. \tag{3.10}$$

The potentials defined above are unique up to a constant. The constants const_i^1, const_i^2 and const_i^3 are determined by the conditions (3.3), (3.7) and (3.10), respectively. We introduce the linear operators M, R and P defined by

$$M(\mathbf{c}) = \nabla\psi^{\mathbf{c}} \quad \text{on } \Omega/\Gamma, \quad R(l) = \nabla\psi^l \quad \text{on } \Omega/\Gamma, \tag{3.11}$$

and

$$P(\boldsymbol{\eta}) = \nabla\psi^{\boldsymbol{\eta}} \quad \text{on}\Omega/\Gamma. \tag{3.12}$$

Next, we define the constant 3×3 tensor σ^∞ by

$$\sigma^{\infty}\mathbf{c} = |\Omega|^{-1}\int_{\partial\Omega}(\nabla\psi^{\mathbf{c}}+\mathbf{c})\cdot\mathbf{n}\,\mathrm{d}s, \tag{3.13}$$

for any $\mathbf{c}$ in R^3 and introduce the surface energy tensor given by

$$\mathscr{G} = -|\Omega|^{-1}\int_{\Gamma}(\mathbf{n}\otimes\mathbf{x})\mathscr{I}\,\mathrm{d}s. \tag{3.14}$$

One argues as in Lipton (1997a) to conclude that σ^{∞} is invertible. It is easily seen that σ^{∞} is precisely the effective conductivity tensor for the case when the pores are filled with a perfect conductor and the matrix has unit conductivity. We denote the 3×3 matrix identity by 'I' and introduce the space of trial fields $\mathscr{U}^{+}$ given by $\mathscr{U}^{+} = \mathscr{P}\times H^1(\Omega_{\mathrm{m}})_{\mathrm{per}}\times H^1(\Gamma)$. The new upper variational principle is given by the following:

Theorem 3.1.

For any prescribed constant heat flux $\bar{\mathbf{p}}$ in R^3

$$(\sigma^{\mathrm{e}})^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} - \gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} + \frac{\alpha\alpha_{\mathrm{T}}^2}{\gamma^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} = |\Omega|^{-1}\max_{((\boldsymbol{\eta},u,q)\,\mathrm{in}\,\mathscr{U}^{+})}\mathscr{L}^{+}(\boldsymbol{\eta},u,q), \tag{3.15}$$

where

$$\begin{aligned}\mathscr{L}^{+}(\boldsymbol{\eta},u,q) &= 2\left(\int_{\Omega}\bar{\mathbf{p}}\cdot\boldsymbol{\eta}\,\mathrm{d}x + \frac{\alpha(-\alpha_{\mathrm{T}})}{\gamma}\int_{\Gamma}\nabla_{\mathrm{s}}q\cdot(\mathrm{I}-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\,\mathrm{d}s\right)\\ &-\int_{\Omega}((\sigma(\mathbf{x}))^{-1}-\gamma^{-1})^{-1}|\boldsymbol{\eta}|^2\,\mathrm{d}x - \alpha\int_{\Gamma}|\nabla_{\mathrm{s}}q|^2\,\mathrm{d}s - (\overset{*}{D})\int_{\Omega_{\mathrm{m}}}|\nabla u|^2\,\mathrm{d}x\\ &-\gamma\int_{\Omega}|M(\sigma^{\infty^{-1}}(\bar{\boldsymbol{\eta}}+\bar{\mathbf{h}})) + R(l) + P(\boldsymbol{\eta}) + \sigma^{\infty^{-1}}(\bar{\boldsymbol{\eta}}+\bar{\mathbf{h}}) - \boldsymbol{\eta}|^2\,\mathrm{d}x.\end{aligned} \tag{3.16}$$

Here, $\overset{*}{\mathrm{D}}$ and α are defined in (2.16), $l = \alpha_{\mathrm{T}}^{-1}q - (\alpha_{\mathrm{C}}/\alpha_{\mathrm{T}})u$ and the vectors $\bar{\boldsymbol{\eta}}$ and $\bar{\mathbf{h}}$ are defined by

$$\bar{\boldsymbol{\eta}} = -|\Omega|^{-1}\int_{\partial\Omega}((\nabla\psi^{\eta}-\boldsymbol{\eta})\cdot\mathbf{n})\mathbf{x}\,\mathrm{d}s, \quad \text{and} \quad \bar{\mathbf{h}} = -|\Omega|^{-1}\int_{\partial\Omega}(\nabla\psi^{l}\cdot\mathbf{n})\mathbf{x}\,\mathrm{d}s. \tag{3.17}$$

This variational principle represents the extension of the variational principle, given in Theorem 3.1 of Lipton (1997) to the case of coupled heat and mass transport on the two-phase interface. We introduce a second equivalent version of this variational principle in Theorem 4.1 of Section 4 that allows for easy comparison with Theorem 3.1 in Lipton (1997). Substitution of simple trial fields into the variational principles given by Theorems 3.1 and 4.1 delivers bounds on the effective conductivity in terms of statistical information on the pore geometry (see Section 5).

Before introducing the lower variational principle we select an isotropic comparison

material with conductivity $\gamma < \sigma_p$ and formulate three auxiliary conductivity problems. For any vector field $\mathbf{p}$ in $L^2(\Omega)^3_{\text{per}}$ we introduce the potential $\phi^{\mathbf{p}}$ in $H^1(\Omega)_{\text{per}}$ which solves

$$[\gamma(\nabla\phi^{\mathbf{p}} + \mathbf{p})] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma_i, \tag{3.18}$$

and

$$-\gamma\Delta\phi^{\mathbf{p}} = \operatorname{div}\mathbf{p} \quad \text{in } \Omega/\Gamma. \tag{3.19}$$

For any vector field $\mathbf{v}$ in $L^2(\Gamma)^3$ we introduce the potentials $\phi^{\mathbf{v}} \in H^1(\Omega)_{\text{per}}$ and $C^{\mathbf{v}} \in H^1(\Omega_m)_{\text{per}}$ that are solutions of:

$$[\gamma(\nabla\phi^{\mathbf{v}})] \cdot \mathbf{n} = (\nabla_s \cdot \mathbf{v} + (\mathbf{v}\cdot\mathbf{n})\mathscr{I}) \quad \text{on } \Gamma_i, \tag{3.20}$$

$$-\gamma\Delta\phi^{\mathbf{v}} = 0 \quad \text{in } \Omega/\Gamma, \tag{3.21}$$

and

$$-\frac{\alpha_C QD}{(-\alpha_T)}\nabla C^{\mathbf{v}} \cdot \mathbf{n} = \alpha_C(\nabla_s \cdot \mathbf{v} + (\mathbf{v}\cdot\mathbf{n})\mathscr{I}) \quad \text{on } \Gamma_i, \tag{3.22}$$

$$\Delta C^{\mathbf{v}} = 0 \quad \text{in } \Omega_m. \tag{3.23}$$

We introduce the linear operators N, S and K defined by

$$N(\mathbf{p}) = \nabla\phi^{\mathbf{p}} \quad \text{on } \Omega, \quad S(\mathbf{v}) = \nabla\phi^{\mathbf{v}} \quad \text{on } \Omega/\Gamma, \tag{3.24}$$

and

$$K(\mathbf{v}) = \nabla C^{\mathbf{v}} \quad \text{on } \Omega_m. \tag{3.25}$$

The operators N and S admit explicit formulas. For any periodic vector $\mathbf{p}$ in $L^2(\Omega)^3_{\text{per}}$, we have $N(\mathbf{p})$ in $L^2(\Omega)^3_{\text{per}}$, where

$$N(\mathbf{p}) = -\frac{1}{\gamma}\sum_{\mathbf{k}\neq 0} e^{\frac{2\pi i\mathbf{k}\cdot\mathbf{x}}{L}} \frac{(\hat{\mathbf{p}}(\mathbf{k})\cdot\mathbf{k})\mathbf{k}}{|\mathbf{k}|^2}, \tag{3.26}$$

and for any vector field $\mathbf{v}$ in $L^2(\Gamma)^3$ we have $S(\mathbf{v})$ in $L^2(\Omega)^3_{\text{per}}$, where

$$S(\mathbf{v}) = -\frac{L}{2\pi i\gamma}\sum_{\mathbf{k}\neq 0} e^{\frac{2\pi i\mathbf{k}\cdot\mathbf{x}}{L}} \frac{\mathbf{k}}{|\mathbf{k}|^2} |\Omega|^{-1} \int_\Gamma e^{\frac{-2\pi i\mathbf{k}\cdot\mathbf{y}}{L}} T\mathbf{v}\, ds. \tag{3.27}$$

Here $T\mathbf{v}$ is given by:

$$T\mathbf{v} = \nabla_s \cdot \mathbf{v} + (\mathbf{v}\cdot\mathbf{n})\mathscr{I}, \tag{3.28}$$

and

$$\hat{\mathbf{p}}(\mathbf{k}) = |\Omega|^{-1} \int_\Omega e^{\frac{-2\pi i\mathbf{k}\cdot\mathbf{x}}{L}} \mathbf{p}(\mathbf{y})\, dy. \tag{3.29}$$

We introduce the space of trials $\mathscr{U}^- = L^2(\Omega)^3_{\text{per}} \times L^2(\Gamma)^3$. The new lower variational principle is given by

Theorem 3.2.

For any prescribed average temperature gradient $\mathbf{E}$ in R^3:

$$(\sigma^e)\mathbf{E}\cdot\mathbf{E} - \gamma\mathbf{E}\cdot\mathbf{E} = |\Omega|^{-1} \max_{((\mathbf{p},\mathbf{v}) \text{ in } \mathscr{U}^-)} \mathscr{L}^-(\mathbf{p},\mathbf{v}), \tag{3.30}$$

where

$$\begin{aligned}\mathscr{L}^-(\mathbf{p},\mathbf{v}) &= 2\left(\int_\Omega \mathbf{p}\cdot\mathbf{E}\,dx + \alpha_T \int_\Gamma \mathbf{v}\cdot(\mathbf{I}-\mathbf{n}\otimes\mathbf{n})\mathbf{E}\,ds\right)\\ &- \int_\Omega ((\sigma(\mathbf{x}))-\gamma)^{-1}|\mathbf{p}|^2\,dx - \frac{(-\alpha_T)}{\alpha_s Q}\int_\Gamma |\mathbf{v}|^2\,ds\\ &- \left(\overset{*}{D}\int_{\Omega_m} |K(\mathbf{v})|^2\,dx + \gamma\int_\Omega |N(\mathbf{p})+\alpha_T S(\mathbf{v})|^2\,dx\right),\end{aligned} \tag{3.31}$$

and $\overset{*}{D}$ is defined in (2.16).

We remark that the operator N is proportional to the projection of $L^2(\Omega)^3_{\text{per}}$ onto the space of periodic curl-free fields. This operator is well known and forms the basis for the Hashin–Shtrikman bounds for anisotropic conductors with perfectly bonded interfaces given by Milton and Kohn (1988). The S operator is the gradient of the simple layer potential with density $T\mathbf{v}$ on the pore–matrix interface.

4. Derivation of the variational principles

Before giving the derivation of the variational principles we given an equivalent statement of the upper variational principle 3.1. We introduce the following 'convex' set of trial fields for ceramics containing N pores:

$$\mathscr{U}_{(u,q)} = \left\{ \begin{array}{c} \psi \in H^1(\Omega)_{\text{per}}, \mathbf{c}\in R^3, \\ \text{and any choice of } N \text{ constants } c_1, c_2, \ldots, c_N, \\ \text{such that } \psi + \mathbf{c}\cdot\mathbf{x} = \alpha_T^{-1} q - \dfrac{\alpha_C}{(-\alpha_T)} u + c_i \quad \text{on } \Gamma_i. \end{array} \right.$$

Theorem 4.1.

For any prescribed constant heat flux $\bar{\mathbf{p}}$ in R^3:

$$(\sigma^e)^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} - \gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} + \frac{\alpha\alpha_T^2}{\gamma^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} = |\Omega|^{-1} \max_{((\boldsymbol{\eta},u,q) \text{ in } \mathscr{U}^+)} \mathscr{L}^+(\boldsymbol{\eta},u,q), \tag{4.1}$$

where $\mathscr{L}^+(\boldsymbol{\eta},u,q)$ admits the alternate formulation given by

$$\mathscr{L}^+(\boldsymbol{\eta},u,q)=2\left(\int_\Omega \bar{\mathbf{p}}\cdot\boldsymbol{\eta}\,\mathrm{d}x+\frac{\alpha(-\alpha_\mathrm{T})}{\gamma}\int_\Gamma \nabla_s q\cdot(\mathrm{I}-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\,\mathrm{d}s\right)$$
$$-\int_\Omega((\sigma(\mathbf{x}))^{-1}-\gamma^{-1})^{-1}|\boldsymbol{\eta}|^2\,\mathrm{d}x-\alpha\int_\Gamma|\nabla_s q|^2\,\mathrm{d}s-(\overset{*}{D})\int_{\Omega_\mathrm{m}}|\nabla u|^2\,\mathrm{d}x$$
$$-\gamma\min_{\mathscr{U}_{(u,q)}}\int_\Omega|\nabla\psi+\mathbf{c}-\boldsymbol{\eta}|^2\,\mathrm{d}x. \tag{4.2}$$

To derive the upper variational principles given by Theorems 3.1 and 4.1 we start with the Thompson variational principle given by Theorem 2.2. Choosing $\gamma>\sigma_\mathrm{m}$ we add and subtract the reference energy $\gamma|\tilde{\mathbf{p}}+\bar{\mathbf{p}}|^2$ to the right-hand-side of (2.15) to obtain

$$(\sigma^\mathrm{e})^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}-\gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}=|\Omega|^{-1}\min_{\tilde{\mathbf{p}}\in V}\left\{\int_\Omega((\sigma(\mathbf{x}))^{-1}-\gamma^{-1})|\tilde{\mathbf{p}}+\bar{\mathbf{p}}|^2\,\mathrm{d}x\right.$$
$$\left.+\gamma^{-1}\int_\Omega|\tilde{\mathbf{p}}|^2\,\mathrm{d}x+2\gamma^{-1}\int_\Omega\tilde{\mathbf{p}}\cdot\bar{\mathbf{p}}\,\mathrm{d}x+\alpha^{-1}\int_\Gamma|\nabla_s g|^2\,\mathrm{d}s+(\overset{*}{D})^{-1}\int_{\Omega_\mathrm{m}}|\nabla w|^2\,\mathrm{d}x\right\}. \tag{4.3}$$

Since $\alpha_\mathrm{T}\Delta_s g=[\tilde{\mathbf{p}}\cdot\mathbf{n}]$, integration by parts gives

$$2\gamma^{-1}\int_\Omega\tilde{\mathbf{p}}\cdot\bar{\mathbf{p}}\,\mathrm{d}x=2\gamma^{-1}\int_\Gamma[\tilde{\mathbf{p}}\cdot\mathbf{n}](\bar{\mathbf{p}}\cdot\mathbf{x})\,\mathrm{d}s=2\gamma^{-1}\int_\Gamma\alpha_\mathrm{T}\Delta_s g(\bar{\mathbf{p}}\cdot\mathbf{x})\,\mathrm{d}s. \tag{4.4}$$

Integration by parts on Γ yields

$$2\gamma^{-1}\int_\Omega\tilde{\mathbf{p}}\cdot\bar{\mathbf{p}}\,\mathrm{d}x=2\gamma^{-1}\int_\Gamma(-\alpha_\mathrm{T})\nabla_s g\cdot(\mathrm{I}-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\,\mathrm{d}s. \tag{4.5}$$

Next we apply (4.5) and complete the square in (4.3) to obtain

$$(\sigma^\mathrm{e})^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}-\gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}+\frac{\alpha\alpha_\mathrm{T}^2}{\gamma^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}=|\Omega|^{-1}\min_{\tilde{\mathbf{p}}\in V}\left\{\int_\Omega((\sigma(\mathbf{x})^{-1}-\gamma^{-1})|\tilde{\mathbf{p}}+\bar{\mathbf{p}}|^2\,\mathrm{d}x\right.$$
$$\left.+\gamma^{-1}\int_\Omega|\mathbf{p}|^2\,\mathrm{d}x+(\overset{*}{D})^{-1}\int_{\Omega_\mathrm{m}}|\nabla w|^2\,\mathrm{d}x+\alpha^{-1}\int_\Gamma\left|\nabla_s g-\frac{\alpha_\mathrm{T}\alpha}{\gamma}(I-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\right|^2\mathrm{d}s\right\}. \tag{4.6}$$

Introducing the bulk and surface polarizations $\boldsymbol{\eta}$ in $\mathscr{P}$, u in $H^1(\Omega_\mathrm{m})_\mathrm{per}$ and q in $H^1(\Gamma)$ we have the elementary estimates

$$\int_\Omega(\sigma(\mathbf{x})^{-1}-\gamma^{-1})|\tilde{\mathbf{p}}+\bar{\mathbf{p}}|^2\,\mathrm{d}x\geqslant 2\int_\Omega(\tilde{\mathbf{p}}+\bar{\mathbf{p}})\cdot\boldsymbol{\eta}\,\mathrm{d}x-\int_\Omega(\sigma(\mathbf{x})^{-1}-\gamma^{-1})^{-1}|\boldsymbol{\eta}|^2\,\mathrm{d}x, \tag{4.7}$$

$$(\overset{*}{D})^{-1}\int_{\Omega_m}|\nabla w|^2\,dx \geqslant 2\int_{\Omega_m}\nabla u\cdot\nabla w\,dx-\overset{*}{D}\int_{\Omega_m}|\nabla u|^2\,dx, \tag{4.8}$$

and

$$\alpha^{-1}\int_\Gamma\left|\nabla_s g-\frac{\alpha_T\alpha}{\gamma}(I-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\right|^2 ds \geqslant 2\int_\Gamma\nabla_s q\cdot\left(\nabla_s g-\frac{\alpha_T\alpha}{\gamma}(I-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\right)ds-\alpha\int_\Gamma|\nabla_s q|^2\,ds. \tag{4.9}$$

Application of these inequalities to (4.6) gives

$$(\sigma^e)^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}-\gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}+\frac{\alpha\alpha_T^2}{\gamma^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} \geqslant |\Omega|^{-1}\min_{\tilde{\mathbf{p}}\in V}\mathscr{M}^+(\tilde{\mathbf{p}},\boldsymbol{\eta},u,q) = |\Omega|^{-1}\mathscr{M}^+(\overset{*}{\tilde{\mathbf{p}}},\boldsymbol{\eta},u,q), \tag{4.10}$$

where $\mathscr{M}^+$ is defined by

$$\begin{aligned}\mathscr{M}^+(\tilde{\mathbf{p}},\boldsymbol{\eta},u,q) &= 2\int_\Omega\bar{\mathbf{p}}\cdot\boldsymbol{\eta}\,dx+2\int_\Gamma\nabla_s q\cdot\left(\frac{(-\alpha_T)\alpha}{\gamma}(I-\mathbf{n}\otimes\mathbf{n})\bar{\mathbf{p}}\right)ds\\ &-\int_\Omega((\sigma(\mathbf{x})^{-1}-\gamma^{-1})^{-1}\boldsymbol{\eta}\cdot\boldsymbol{\eta}\,dx-\overset{*}{D}\int_{\Omega_m}|\nabla u|^2\,dx-\alpha\int_\Gamma|\nabla_s q|^2\,ds\\ &+2\int_\Omega\tilde{\mathbf{p}}\cdot\boldsymbol{\eta}\,dx+2\int_{\Omega_m}\nabla u\cdot\nabla w\,dx+2\int_\Gamma\nabla_s q\cdot\nabla_s g\,ds+\gamma^{-1}\int_\Omega|\tilde{\mathbf{p}}|^2\,dx\end{aligned} \tag{4.11}$$

and $\overset{*}{\tilde{\mathbf{p}}}$ is the minimizer of

$$\mathscr{T}=\min_{\tilde{\mathbf{p}}\in V}\left\{2\int_\Omega\tilde{\mathbf{p}}\cdot\boldsymbol{\eta}\,dx+2\int_{\Omega_m}\nabla u\cdot\nabla w\,dx+2\int_\Gamma\nabla_s q\cdot\nabla_s g\,ds+\gamma^{-1}\int_\Omega|\tilde{\mathbf{p}}|^2\,dx\right\}. \tag{4.12}$$

Since $\alpha_T\Delta_s g=[\tilde{\mathbf{p}}\cdot\mathbf{n}]$ and $-\nabla w\cdot\mathbf{n}=(\alpha_C/\alpha_T)[\tilde{\mathbf{p}}\cdot\mathbf{n}]$, integration by parts in the middle two terms in (4.12) gives

$$\mathscr{T}=\min_{\tilde{\mathbf{p}}\in V}\left\{\int_\Omega 2\tilde{\mathbf{p}}\cdot\boldsymbol{\eta}\,dx+2\int_\Gamma\left((-\alpha_T)^{-1}q+\frac{\alpha_C}{\alpha_T}u\right)[\tilde{\mathbf{p}}\cdot\mathbf{n}]\,ds+\gamma^{-1}\int_\Omega|\tilde{\mathbf{p}}|^2\,dx\right\}. \tag{4.13}$$

Taking the first variation, one finds that the minimizer is given by

$$\overset{*}{\tilde{\mathbf{p}}}=\gamma(\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta}), \tag{4.14}$$

where $\overset{*}{\psi}$ is in $H^1(\Omega)_{per}$ and $\overset{*}{\mathbf{c}}$ is a constant vector. The function $\overset{*}{\psi}$ and the constant vector $\overset{*}{\mathbf{c}}$, together with N constants $\overset{*}{c}_1,\overset{*}{c}_2,\ldots,\overset{*}{c}_N$ is the solution of the system

$$\overset{*}{\psi}+\overset{*}{\mathbf{c}}\cdot\mathbf{x}=l+\overset{*}{c}_i \quad \text{on } \Gamma_i,$$

$$\nabla\cdot(\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta})=0 \quad \text{on } \Omega/\Gamma,$$

$$\int_{\Gamma_i}[(\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta})]\cdot\mathbf{n}\,\mathrm{d}s=0,$$

and

$$\int_{\partial\Omega}(\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta})\cdot\mathbf{n}\mathbf{x}\,\mathrm{d}s=0, \tag{4.15}$$

where $l=(\alpha_{\mathrm{T}})^{-1}q-(\alpha_{\mathrm{C}}/\alpha_{\mathrm{T}})u$. To solve for $\overset{*}{\psi}$, $\mathbf{c}$ and $\overset{*}{c}_1,\ldots,\overset{*}{c}_N$ simultaneously in (4.15) we make use of the linearity inherent in the problem and form the three auxiliary problems given by (3.1)–(3.10). One readily sees that the choice

$$\overset{*}{\mathbf{c}}=\boldsymbol{\sigma}^{\infty-1}(\bar{\boldsymbol{\eta}}+\bar{\mathbf{h}}) \tag{4.16}$$

and $\overset{*}{\psi}=\psi^{\mathbf{c}}+\psi^{l}+\psi^{\boldsymbol{\eta}}$ is the solution to the system (4.15). Recalling the definitions of the operators M, R and P we have the inequality

$$(\sigma^{\mathrm{e}})^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}-\gamma^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}+\frac{\alpha\alpha_{\mathrm{T}}^2}{\gamma^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}}\geqslant|\Omega|^{-1}\max_{(\boldsymbol{\eta},u,q)}\mathscr{M}^{+}(\overset{*}{\bar{\mathbf{p}}},\boldsymbol{\eta},u,q)$$

$$=|\Omega|^{-1}\max_{(\boldsymbol{\eta},u,q)}\mathscr{L}^{+}(\boldsymbol{\eta},u,q). \tag{4.17}$$

For the choice of bulk and surface polarizations, consistent with the actual heat flux, volumetric concentration flux and surface concentration in the porous ceramic, i.e.,

$$q=C_{\mathrm{s}}(\varphi,C)-\frac{(-\alpha_{\mathrm{T}})}{\gamma}\bar{\mathbf{p}}\cdot\mathbf{x}$$

$$=\alpha_{\mathrm{T}}(\tilde{\varphi}+\mathbf{E}\cdot\mathbf{x})+\alpha_{\mathrm{C}}C-\frac{(\alpha_{\mathrm{T}})}{\gamma}\bar{\mathbf{p}}\cdot\mathbf{x}$$

$$\nabla u=\nabla C, \tag{4.18}$$

and

$$\boldsymbol{\eta}=(\sigma(\mathbf{x})^{-1}-\gamma^{-1})(\sigma(\mathbf{x})(\nabla\tilde{\varphi}+\mathbf{E})),$$

where $\mathbf{E}=\sigma^{\mathrm{e}-1}\bar{\mathbf{p}}$, we find that $\overset{*}{\psi}=\tilde{\varphi}$, $\overset{*}{\mathbf{c}}=(\boldsymbol{\sigma}^{\mathrm{e}-1}-\gamma^{-1})\bar{\mathbf{p}}$ and (4.17) holds with equality. This establishes Theorem 3.1. To establish Theorem 4.1 we evaluate $\mathscr{T}$ at the minimizer $\overset{*}{\bar{\mathbf{p}}}$ and write

$$\mathscr{T}=\gamma\int_{\Omega}|\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta}|^2\,\mathrm{d}x, \tag{4.19}$$

where $\overset{*}{\mathbf{c}}$ is given by (4.16). We show

$$\int_\Omega |\nabla \overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta}|^2\,\mathrm{d}x = \min_{\mathscr{U}_{(u,q)}} \int_\Omega |\nabla\psi+\mathbf{c}-\boldsymbol{\eta}|^2\,\mathrm{d}x. \tag{4.20}$$

Indeed, for any choice ψ, $\mathbf{c}$ and $c_1,\ldots,c_N$ in $\mathscr{U}_{(u,q)}$ we write $\psi=\overset{*}{\psi}+\delta\psi$, $\mathbf{c}=\overset{*}{\mathbf{c}}+\boldsymbol{\delta}\mathbf{c}$, $c_i=\overset{*}{c}_i+\delta c_i$. The variations satisfy $\delta\psi+\delta\mathbf{c}\cdot\mathbf{x}=\delta c_i$ on Γ_i. We have

$$\int_\Omega |\nabla\psi+\mathbf{c}-\boldsymbol{\eta}|^2\,\mathrm{d}x = \int_\Omega |\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta}|^2\,\mathrm{d}x+\int_\Omega |\nabla\delta\psi+\delta\mathbf{c}|^2\,\mathrm{d}x$$
$$+2\int_\Omega (\nabla\delta\psi+\delta\mathbf{c})\cdot(\nabla\overset{*}{\psi}+\overset{*}{\mathbf{c}}-\boldsymbol{\eta})\,\mathrm{d}x. \tag{4.21}$$

Since $\overset{*}{\psi}$, $\overset{*}{\mathbf{c}}$ and $\overset{*}{c}_i$ is the solution to (4.15), the last term of (4.21) vanishes and Theorem 4.1 follows.

Next we establish Theorem 3.2 for the choice of isotropic comparison material $\gamma<\sigma_{\mathrm{p}}$. Starting with the Dirichlet-like variational principle given by Theorem 2.1 we add and subtract the reference energy $\gamma|\nabla\varphi+\mathbf{E}|^2$ to obtain

$$\sigma^{\mathrm{e}}\mathbf{E}\cdot\mathbf{E}-\gamma\mathbf{E}\cdot\mathbf{E} = |\Omega|^{-1}\min_{(\varphi,\mathscr{C})\in U}\left\{\int_\Omega(\sigma(\mathbf{x})-\gamma)|\nabla\varphi+\mathbf{E}|^2\,\mathrm{d}x\right.$$
$$\left.+\gamma\int_\Omega|\nabla\varphi|^2\,\mathrm{d}x+\frac{\alpha_{\mathrm{C}}QD}{(-\alpha_{\mathrm{T}})}\int_{\Omega_{\mathrm{m}}}|\nabla\mathscr{C}|^2\,\mathrm{d}x+\frac{\alpha_{\mathrm{s}}Q}{(-\alpha_{\mathrm{T}})}\int_\Gamma|\nabla_{\mathrm{s}}C_{\mathrm{s}}(\varphi,\mathscr{C})|^2\,\mathrm{d}s\right\}. \tag{4.22}$$

One has the elementary estimates

$$\int_\Omega(\sigma(\mathbf{x})-\gamma)|\nabla\varphi+\mathbf{E}|^2\,\mathrm{d}x\geqslant 2\int_\Omega\mathbf{p}\cdot(\nabla\varphi+\mathbf{E})\,\mathrm{d}x-\int_\Omega(\sigma(\mathbf{x})-\gamma)^{-1}|\mathbf{p}|^2\,\mathrm{d}x, \tag{4.23}$$

and

$$\frac{\alpha_{\mathrm{s}}Q}{(-\alpha_{\mathrm{T}})}\int_\Gamma|\nabla_{\mathrm{s}}C_{\mathrm{s}}(\varphi,\mathscr{C})|^2\,\mathrm{d}s\geqslant 2\int_\Gamma\mathbf{v}\cdot\nabla_{\mathrm{s}}C_{\mathrm{s}}\,\mathrm{d}s-\frac{(-\alpha_{\mathrm{T}})}{\alpha_{\mathrm{s}}Q}\int_\Gamma|\mathbf{v}|^2\,\mathrm{d}s, \tag{4.24}$$

for all polarizations $\mathbf{p}$ in $L^2(\Omega)^3_{\mathrm{per}}$ and $\mathbf{v}$ in $L^2(\Gamma)^3$. Application of these inequalities to (4.22) gives

$$\sigma^{\mathrm{e}}\mathbf{E}\cdot\mathbf{E}-\gamma\mathbf{E}\cdot\mathbf{E}\geqslant|\Omega|^{-1}\min_{(\varphi,\mathscr{C})\in U}\mathscr{M}^-(\mathbf{p},\mathbf{v},\varphi,\mathscr{C})=|\Omega|^{-1}\mathscr{M}^-(\mathbf{p},\mathbf{v},\overset{*}{\varphi},\overset{*}{\mathscr{C}}), \tag{4.25}$$

where $\mathscr{M}^-(\mathbf{p},\mathbf{v},\varphi,\mathscr{C})$ is defined by

$$\mathscr{M}^-(\mathbf{p},\mathbf{v},\varphi,\mathscr{C})=2\int_\Omega\mathbf{p}\cdot\mathbf{E}\,\mathrm{d}x+2\alpha_{\mathrm{T}}\int_\Gamma\mathbf{v}\cdot\nabla_{\mathrm{s}}(\mathbf{E}\cdot\mathbf{x})\,\mathrm{d}s$$
$$-\int_\Omega(\sigma(\mathbf{x})-\gamma)^{-1}|\mathbf{p}|^2\,\mathrm{d}x-\frac{(-\alpha_{\mathrm{T}})}{\alpha_{\mathrm{s}}Q}\int_\Gamma|\mathbf{v}|^2\,\mathrm{d}s$$

$$+2\int_\Gamma \mathbf{v}\cdot(\alpha_T\nabla_s\varphi)\,ds+2\int_\Gamma \mathbf{v}\cdot(\alpha_C\nabla_s\mathscr{C})\,ds+2\int_\Omega \mathbf{p}\cdot\nabla\varphi\,dx$$
$$+\frac{\alpha_C QD}{(-\alpha_T)}\int_{\Omega_m}|\nabla\mathscr{C}|^2\,dx+\gamma\int_\Omega|\nabla\varphi|^2\,dx, \tag{4.26}$$

and $(\varphi^*,\mathscr{C}^*)$ is the minimizer of

$$\mathscr{W}=\min_{\varphi,\mathscr{C}}\left\{2\int_\Gamma \mathbf{v}\cdot(\alpha_T\nabla_s\varphi)\,ds+2\int_\Gamma \mathbf{v}\cdot(\alpha_C\nabla_s\mathscr{C})\,ds+2\int_\Omega \mathbf{p}\cdot\nabla\varphi\,dx\right.$$
$$\left.+\frac{\alpha_C QD}{(-\alpha_T)}\int_{\Omega_m}|\nabla\mathscr{C}|^2\,dx+\gamma\int_\Omega|\nabla\varphi|^2\,dx\right\}. \tag{4.27}$$

Taking the first variation one finds that the minimizer $(\varphi^*,\mathscr{C}^*)$ is the solution of

$$\gamma\Delta\varphi^*=-\operatorname{div}\mathbf{p}\quad\text{in }\Omega/\Gamma, \tag{4.28}$$

$$[\gamma\nabla\varphi^*+\mathbf{p}]\cdot\mathbf{n}=\nabla_s\cdot\mathbf{v}+(\mathbf{v}\cdot\mathbf{n})\mathscr{I}\quad\text{on }\Gamma_i, \tag{4.29}$$

and

$$\Delta\mathscr{C}^*=0\quad\text{in }\Omega_m, \tag{4.30}$$

$$-\frac{QD}{(-\alpha_T)}\mathbf{n}\cdot\nabla\mathscr{C}^*=\nabla_s\cdot\mathbf{v}+(\mathbf{v}\cdot\mathbf{n})\mathscr{I}\quad\text{on }\Gamma_i. \tag{4.31}$$

Since (4.28) and (4.29) are linear we write $\varphi^*=\varphi^{\mathbf{p}}+\varphi^{\mathbf{v}}$ where both $\varphi^{\mathbf{p}}$ and $\varphi^{\mathbf{v}}$ are elements of $H^1(\Omega)_{\text{per}}$ and

$$\gamma\Delta\varphi^{\mathbf{p}}=-\operatorname{div}\mathbf{p}\quad\text{in }\Omega/\Gamma,\quad[\gamma\nabla\varphi^{\mathbf{p}}+\mathbf{p}]\cdot\mathbf{n}=0\quad\text{on }\Gamma_i, \tag{4.32}$$

and

$$\gamma\Delta\varphi^{\mathbf{v}}=0\quad\text{in }\Omega/\Gamma,\quad[\gamma\nabla\varphi^{\mathbf{v}}]\cdot\mathbf{n}=\nabla_s\cdot\mathbf{v}+(\mathbf{v}\cdot\mathbf{n})\mathscr{I}\quad\text{on }\Gamma_i. \tag{4.33}$$

Writing $N(\mathbf{p})=\nabla\varphi^{\mathbf{p}}$, $S(\mathbf{v})=\nabla\varphi^{\mathbf{v}}$, $K(\mathbf{v})=\nabla\mathscr{C}^*$ and observing that $\nabla_s(\mathbf{E}\cdot\mathbf{x})=(\mathrm{I}-\mathbf{n}\otimes\mathbf{n})\mathbf{E}$ on Γ we have the inequality

$$\sigma^e\mathbf{E}\cdot\mathbf{E}-\gamma\mathbf{E}\cdot\mathbf{E}\geqslant|\Omega|^{-1}\max_{(\mathbf{p},\mathbf{v})}\mathscr{M}^-(\mathbf{p},\mathbf{v},\varphi^*,\mathscr{C}^*)=|\Omega|^{-1}\max_{(\mathbf{p},\mathbf{v})}\mathscr{L}^-(\mathbf{p},\mathbf{v}). \tag{4.34}$$

Equality in (4.34) holds when the polarizations $(\mathbf{p},\mathbf{v})$ correspond to the actual fields in the porous ceramic given by

$$\mathbf{p}=(\sigma(\mathbf{x})-\gamma)(\nabla\tilde{\varphi}+\mathbf{E})\quad\text{and}\quad\mathbf{v}=\frac{\alpha_s Q}{(-\alpha_T)}\nabla_s C_s(\tilde{\varphi},C). \tag{4.35}$$

The explicit representation of the operator S given by (3.27) is derived in Lipton (1997a). The representation of the operator N given by (3.26) is well known and the derivation is provided in Milton and Kohn (1988).

5. Upper bounds and energy dissipation inequalities

In this section Theorem 3.1 is applied to obtain upper bounds and energy dissipation inequalities for the effective conductivity tensor. Explicit upper bounds are given for the effective conductivity tensor for anisotropic porous materials: see Theorem 5.2. For isotropic composites we present an upper bound given in terms of the specific surface area of the pore–matrix interface: see Theorem 5.3. The upper energy dissipation inequality is given in Theorem 5.4. Theorems 5.5 and 5.6 give bounds on their effective conductivity in terms of statistical information on the pore geometry.

The region occupied by the ith pore is denoted by B_i and its boundary by Γ_i. We set $\gamma = \sigma_{\rm m}$ and choose trial polarizations of the form $\boldsymbol{\eta} = \chi_{\rm p}\boldsymbol{\mu}$ and $q = \mathbf{r}\cdot\mathbf{x}$, on each pore surface. Here $\chi_{\rm p}$ is the indicator function for the pore phase, i.e., $\chi_{\rm p}(\mathbf{x}) = 1$ for $\mathbf{x}$ in the pore phase and zero otherwise. The trial polarization $u \in H^1(\Omega_{\rm m})_{\rm per}$ is taken to be the solution of the boundary value problem.

$$\Delta u = 0 \quad \text{in} \quad \Omega_{\rm m}, \quad \mathrm{u} = \mathbf{b}\cdot\mathbf{x} + \mathrm{const}_i \quad \text{on } \Gamma_i, \tag{5.1}$$

and

$$\int_{\Gamma_i} (-\mathbf{n}\cdot\nabla u)\,\mathrm{d}s = 0.$$

Here $\boldsymbol{\mu}$, $\mathbf{r}$ and $\mathbf{b}$ are vectors in R^3. The associated bound is given by the Theorem below.

Theorem 5.1.

For any prescribed constant heat flux $\bar{\mathbf{p}}$ in R^3 we have the following:

$$(\sigma^{\rm e})^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} - \sigma_{\rm m}^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} + \frac{\alpha\alpha_{\rm T}^2}{\sigma_{\rm m}^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} \geqslant \max_{(\boldsymbol{\mu},\mathbf{b},\mathbf{r})} \{2\bar{L}(\bar{\mathbf{p}},\boldsymbol{\mu},\mathbf{r}) - \bar{Q}(\boldsymbol{\mu},\mathbf{b},\mathbf{r})\}, \tag{5.2}$$

where

$$\bar{L}(\bar{\mathbf{p}},\boldsymbol{\mu},\mathbf{r}) = \theta_{\rm p}\bar{\mathbf{p}}\cdot\boldsymbol{\mu} - \frac{(-\alpha_{\rm T})\alpha}{\sigma_{\rm m}}\mathscr{G}\mathbf{r}\cdot\bar{\mathbf{p}}, \tag{5.3}$$

and

$$\bar{Q}(\boldsymbol{\mu},\mathbf{b},\mathbf{r}) = \theta_{\rm p}(\sigma_{\rm m}+\lambda)|\boldsymbol{\mu}|^2 - 2\sigma_{\rm m}\theta_{\rm p}\left(\alpha_{\rm T}^{-1}\mathbf{r} - \frac{\alpha_{\rm C}}{\alpha_{\rm T}}\mathbf{b}\right)\cdot\boldsymbol{\mu} + \alpha\mathscr{G}\mathbf{r}\cdot\mathbf{r} + \overset{*}{D}(\sigma^{\infty}$$
$$-(1+\theta_{\rm p})\mathrm{I})\mathbf{b}\cdot\mathbf{b} + \sigma_{\rm m}(\mathrm{I}-(\sigma^{\infty})^{-1})\left(\alpha_{\rm T}^{-1}\mathbf{r} - \frac{\alpha_{\rm C}}{\alpha_{\rm T}}\mathbf{b}\right)\cdot\left(\alpha_{\rm T}^{-1}\mathbf{r} - \frac{\alpha_{\rm C}}{\alpha_{\rm T}}\mathbf{b}\right). \tag{5.4}$$

Here $\lambda = (\sigma_p^{-1} - \sigma_m^{-1})^{-1}$ and σ^∞ is the effective conductivity tensor of a composite with perfectly conducting pores, having the same geometry as the original composite, embedded in a matrix of unit conductivity.

Proof: We observe that (5.3), follows immediately upon substitution of the polarizations into (3.16). To obtain $\bar{Q}$, given by (5.4), we solve the auxiliary problems (3.1)–(3.10). We find that $\psi^\eta = \text{const}$ inside the composite and ψ^l is the solution of

$$\Delta\psi^l = 0 \quad \text{in } \Omega_m, \quad \psi^l = \alpha_s^{-1}\mathbf{r}\cdot\mathbf{x} - (\alpha_C/\alpha_T)\mathbf{b}\cdot\mathbf{x} + \text{const}_i \quad \text{on } \Gamma_i, \tag{5.5}$$

and

$$\int_{\Gamma_i} [\nabla\psi^l \cdot \mathbf{n}]\, ds = 0.$$

Inspection shows that ψ^l is linear inside each pore, i.e., $\psi^l = \alpha_s^{-1}\mathbf{r}\cdot\mathbf{x} - (\alpha_C/\alpha_T)\mathbf{b}\cdot\mathbf{x} + \text{const}_i$ in B_i. From the definition of σ^∞ it follows that

$$\bar{\mathbf{h}} = |\Omega|^{-1} \int_{\partial\Omega} (\nabla\psi^l \cdot \mathbf{n})\mathbf{x}\, ds = (\sigma^\infty - \mathrm{I})(\alpha_s^{-1}\mathbf{r} - (\alpha_C/\alpha_T)\mathbf{b}). \tag{5.6}$$

Since $\bar{\boldsymbol{\eta}} = 0$ it follows from (4.16) that

$$\bar{\mathbf{c}}^* = \sigma^{\infty^{-1}}\bar{\mathbf{h}} = (\mathrm{I} - \sigma^{\infty^{-1}})(\alpha_s^{-1}\mathbf{r} - (\alpha_C/\alpha_T)\mathbf{b}). \tag{5.7}$$

A lengthy but straightforward application of (5.5)–(5.7), delivers

$$\begin{aligned}
&\sigma_m|\Omega|^{-1} \int_\Omega |M(\sigma^{\infty^{-1}}(\bar{\boldsymbol{\eta}} + \bar{\mathbf{h}})) + R(l) + P(\boldsymbol{\eta}) + \sigma^{\infty^{-1}}(\bar{\boldsymbol{\eta}} + \bar{\mathbf{h}}) - \boldsymbol{\eta}|^2\, dx \\
&= \sigma_m \left\{ \theta_p|\boldsymbol{\mu}|^2 - 2\theta_p \left(\alpha_T^{-1}\mathbf{r} - \frac{\alpha_C}{\alpha_T}\mathbf{b}\right)\cdot\boldsymbol{\mu} \right. \\
&\left. + (\mathrm{I} - (\sigma^\infty)^{-1}) \left(\alpha_T^{-1}\mathbf{r} - \frac{\alpha_C}{\alpha_T}\mathbf{b}\right)\cdot\left(\alpha_T^{-1}\mathbf{r} - \frac{\alpha_C}{\alpha_T}\mathbf{b}\right) \right\}.
\end{aligned} \tag{5.8}$$

Noting that u is a solution to (5.1) one obtains

$$\int_{\Omega_m} |\nabla u|^2\, dx = |\Omega|(\sigma^\infty - (1+\theta_p)\mathrm{I})\mathbf{b}\cdot\mathbf{b}, \tag{5.9}$$

and the theorem follows.

Optimization over all choices of $\boldsymbol{\mu}$, $\mathbf{b}$ and $\mathbf{r}$ gives the following explicit upper bounds on the effective conductivity tensor for anisotropic porous ceramics.

Theorem 5.2.

For any prescribed constant heat flux $\bar{\mathbf{p}}$ in R^3:

$$(\sigma^e)^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} \geqslant \sigma_m^{-1}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} - \frac{\alpha\alpha_T^2}{\sigma_m^2}\mathscr{G}\bar{\mathbf{p}}\cdot\bar{\mathbf{p}} + \begin{pmatrix} A & B & C \\ B & D & E \\ C & E & F \end{pmatrix}^{-1} \begin{bmatrix} \theta_p\bar{\mathbf{p}} \\ \dfrac{(-\alpha_T)\alpha\mathscr{G}}{\sigma_m}\bar{\mathbf{p}} \\ 0 \end{bmatrix} \cdot \begin{bmatrix} \theta_p\bar{\mathbf{p}} \\ \dfrac{(-\alpha_T)\alpha\mathscr{G}}{\sigma_m}\bar{\mathbf{p}} \\ 0 \end{bmatrix}, \quad (5.10)$$

where the 3×3 symmetric matrices A, B, C, D, E and F are given by

$$A = \theta_p(\lambda+\sigma_m)I,$$

$$B = -\sigma_m\theta_p\alpha_T^{-1}I,$$

$$C = -\sigma_m\theta_p\cdot\frac{\alpha_C}{(-\alpha_T)}I,$$

$$D = \alpha\mathscr{G} + \sigma_m\alpha_T^{-2}(I-\sigma^{\infty-1}),$$

$$E = \sigma_m\left(\frac{-\alpha_C}{\alpha_T^2}\right)(I-\sigma^{\infty-1}),$$

$$F = \overset{*}{D}(\sigma^\infty - (1+\theta_p)I) + \sigma_m\left(\frac{\alpha_C}{\alpha_T}\right)^2(I-\sigma^{\infty-1}). \quad (5.11)$$

For isotropic composites the surface energy tensor is $\mathscr{G} = \frac{2}{3}(s/|\Omega|)I$, where s is the surface area of the pore–matrix interface. The specific surface area $\tilde{s}$ is given by $\tilde{s} = (s/|\Omega|)$. We introduce the rational function

$$UB(x,y) \overset{def}{=} \frac{\sigma_m(\theta_p x + \sigma_m(1-y))}{\theta_p xy + \sigma_m(1-y)}, \quad (5.12)$$

where $UB(x,y)$ is defined for the variables x, y in the domain given by

$$-(\sigma_m-\sigma_p) \leqslant x < \infty, 0 \leqslant y \leqslant \frac{1}{1+\dfrac{3\theta_p}{\theta_m}}. \quad (5.13)$$

For x, y in the domain, the function UB is decreasing in y and increasing in x. We introduce the dimensionless constants

$$A_{\mathrm{T}} = \frac{(-\alpha_{\mathrm{T}})\alpha_{\mathrm{s}} Q}{\sigma_{\mathrm{m}} - \sigma_{\mathrm{p}}} \frac{\tilde{s}}{3\theta_{\mathrm{p}}}, \quad A_{\mathrm{C}} = \frac{\alpha_{\mathrm{C}}\alpha_{\mathrm{s}}}{D} \frac{\tilde{s}}{3\theta_{\mathrm{p}}} \left(\frac{\sigma^{\infty} - 1}{\theta_{\mathrm{p}}} - 1 \right)^{-1}. \tag{5.14}$$

We introduce the variable Z defined by

$$Z = (\sigma_{\mathrm{m}} - \sigma_{\mathrm{p}}) \left(\frac{2A_{\mathrm{T}}}{1 + 2A_{\mathrm{C}}} - 1 \right), \tag{5.15}$$

and the upper bound for statistically isotropic porous ceramics is given by:

Theorem 5.3. Upper bound on the effective conductivity tensor for statistically isotropic porous ceramics.

$$\sigma^{\mathrm{e}} \leqslant UB(Z, (\sigma^{\infty})^{-1}). \tag{5.16}$$

For isotropic polydisperse suspensions of spheres $\tilde{s} = 3\theta_{\mathrm{p}}\langle a^{-1} \rangle$ and Theorem 1.1 of Section 1 follows immediately.

We observe that $UB(0, (\sigma^{\infty})^{-1}) = \sigma_{\mathrm{m}}$ and from monotonicity we obtain:

Theorem 5.4. Upper energy dissipation inequality for isotropic suspensions of pores.

For any value of the pore volume fraction θ_{p}:
If

$$\frac{2A_{\mathrm{T}}}{1 + 2A_{\mathrm{C}}} \leqslant 1, \tag{5.17}$$

then

$$\sigma^{\mathrm{e}} \leqslant \sigma_{\mathrm{m}}.$$

It is evident from (5.15) that the parameter Z increases with σ^{∞} and we indicate the dependence by writing $Z = Z(\sigma^{\infty})$. One easily checks that the upper bound

$$UB(Z(\sigma^{\infty}), (\sigma^{\infty})^{-1})$$

is increasing with σ^{∞} and it follows that any upper bound $\bar{\sigma}$ on σ^{∞} delivers an upper bound on the effective conductivity of the form $UB(Z(\bar{\sigma}), (\bar{\sigma})^{-1})$. We consider suspensions of spherical pores of different radius for a given value of the geometric parameter 'q'. Here 'q' is defined to be the minimum, over all pores, of the ratio of pore radius to the distance from the pore center to the nearest neighbor in the suspension. For this case one has the upper bound on σ^{∞} derived by Bruno (1991). This bound is written

$$\sigma^{\infty} \leqslant W(\infty) = \frac{S_{\mathrm{M}}}{S_{\mathrm{m}}} \left(1 + \frac{\left(1 - \dfrac{\theta_{\mathrm{p}}}{\delta} \right)^2}{(1 - \theta_{\mathrm{p}}/\delta)(-S_{\mathrm{M}}/\delta) + (\theta_{\mathrm{p}}/\delta^2)((\theta_{\mathrm{m}}/3) - S_{\mathrm{m}})} \right). \tag{5.18}$$

Here $\delta = S_{\mathrm{M}} - S_{\mathrm{m}}$, where $S_{\mathrm{m}} = (1/3)(1 - q^3)$ and $S_{\mathrm{M}} = A/(1 + A)$. The parameter A is a function of q and can be determined numerically as shown in Appendix A of Bruno

(1991). Estimating σ^{∞} using (5.18) delivers an upper bound in terms of pore volume fraction, pore size distribution $\langle a^{-1}\rangle$ and 'q' given by:

Theorem 5.5. Upper bound for the effective conductivity of a polydisperse suspension of spherical pores with statistically specified pore microstructure.

$$\sigma^{e} \leqslant UB(Z(W(\infty)), W(\infty)^{-1}),$$

where

$$Z(W(\infty)) = \frac{\sigma_m - \sigma_p}{1 + \dfrac{2\alpha_s\alpha_C\theta_p\langle a^{-1}\rangle}{D(W(\infty)-(1+\theta_p))}}\left(\frac{2Q(-\alpha_T)\alpha_s\langle a^{-1}\rangle}{(\sigma_m-\sigma_p)} - 1 - \frac{2\alpha_s\alpha_C\theta_p\langle a^{-1}\rangle}{D(W(\infty)-(1+\theta_p))}\right), \quad (5.19)$$

and the upper bound function UB is given by (5.12).

For monodisperse suspensions of spherical pores of radius a with a prescribed nearest neighbor distribution function $H(x)$, the upper bound on σ^{∞} is given by the security sphere bound developed by Torquato and Rubinstein (1991). This bound is given by

$$\sigma^{\infty} \leqslant J(H) = 1 + 2a\theta_p\int_1^{\infty}\frac{3x^3}{x^3-1}H(x)\,dx. \quad (5.20)$$

Here $H(r)\,dr$ is the probability that a given sphere of diameter $2a$ at the origin, has a nearest neighbor with the center lying at a distance between r and $r+dr$ from its boundary. Estimation of σ^{∞} using (5.20) delivers an upper bound in terms of pore volume fraction, pore size and the nearest neighbor distribution function '$H(x)$'. The upper bound is given by the following formula.

Theorem 5.6. Upper bound for the effective conductivity of a monodisperse suspension of spherical pores with statistically specified pore microstructure.

$$\sigma^{e} \leqslant UB(Z(J(H)), J(H)^{-1}),$$

where

$$Z(J(H)) = \frac{\sigma_m - \sigma_p}{1 + \dfrac{2\alpha_s\alpha_C\theta_p a^{-1}}{D(J(H)-(1+\theta_p))}}\left(\frac{2Q(-\alpha_T)\alpha_s a^{-1}}{(\sigma_m-\sigma_p)} - 1 - \frac{2\alpha_s\alpha_C\theta_p a^{-1}}{D(J(H)-(1+\theta_p))}\right). \quad (5.21)$$

6. Lower bounds and energy dissipation inequalities

In this section we make specific choices of trial fields in Theorem 3.2 to obtain lower bounds and energy dissipation inequalities for the effective conductivity tensor.

Explicit lower bounds are given for the effective conductivity tensor for anisotropic porous materials: see Theorems 6.2 and 6.5. For isotropic composites we present a lower bound given in terms of the average surface to volume dissipation over the pores: see Theorem 6.6. The lower energy dissipation inequality is given in Theorem 6.7. Theorems 6.8 and 6.9 give bounds on the effective conductivity in terms of statistical information on the pore geometry.

We make a choice of trial fields for which the integrals appearing in the variational principle are easy to compute or estimate for any particle shape. We choose $\mathbf{p} = \chi_m \boldsymbol{\mu}$ where $\boldsymbol{\mu}$ is a vector in R^3 and χ_m is the indicator function for the matrix phase, i.e., $\chi_m(\mathbf{x}) = 1$ for $\mathbf{x}$ in the matrix phase and zero otherwise. For $\mathbf{r}$ in R^3 we introduce the polarization $\mathbf{v} = \nabla_s \phi^j r_j$ on the surface of each pore, where r_j are the components of the vector $\mathbf{r}$ and

$$\Delta_s \phi^j = -n_j \quad \text{on } \Gamma_i, \tag{6.1}$$

and

$$\Delta \phi^j = 0 \quad \text{in the pore } B_i.$$

Here n_j is the jth component of the outward unit normal to the pore–matrix interface. We set $\gamma = \sigma_p$ and substitute these trial fields into Theorem 3.2 to find the following:

Theorem 6.1.

For any prescribed constant temperature gradient $\mathbf{E}$ in R^3

$$\sigma^e \mathbf{E}\cdot\mathbf{E} - \sigma_p \mathbf{E}\cdot\mathbf{E} \geqslant \max_{(\boldsymbol{\mu},\mathbf{r})} \{2\underline{L}(\mathbf{E},\boldsymbol{\mu},\mathbf{r}) - \underline{\underline{Q}}(\boldsymbol{\mu},\mathbf{r})\}, \tag{6.2}$$

where

$$\underline{L}(\mathbf{E},\boldsymbol{\mu},\mathbf{r}) = \theta_m \mathbf{E}\cdot\boldsymbol{\mu} + \alpha_T \theta_p \mathbf{E}\cdot\mathbf{r} \tag{6.3}$$

and

$$\underline{\underline{Q}}(\boldsymbol{\mu},\mathbf{r}) = (\alpha_T)^2 (\sigma_p^{-1}\mathrm{G} + \mathrm{L})\mathbf{r}\cdot\mathbf{r} - 2(\alpha_T)\sigma_p^{-1}\mathrm{G}\mathbf{r}\cdot\boldsymbol{\mu}((\sigma_m - \sigma_p)^{-1}\theta_m \mathrm{I} + \sigma_p^{-1}\mathrm{G})\boldsymbol{\mu}\cdot\boldsymbol{\mu}. \tag{6.4}$$

Here L is given by

$$\mathrm{L} = \frac{1}{Q\alpha_s(-\alpha_T)}\mathrm{U} + \frac{\alpha_C}{(-\alpha_T)QD}(\sigma_m \mathrm{I} - \sigma^0), \tag{6.5}$$

where for N pores, U is a matrix of interfacial parameters given by

$$\mathrm{U}_{kl} = |\Omega|^{-1} \sum_{i=1}^{N} \int_{\Gamma_i} \nabla_s \phi^k \cdot \nabla_s \phi^l \, \mathrm{d}s. \tag{6.6}$$

For a prescribed constant temperature gradient $\mathbf{r}$, the matrix σ^0 is given by

$$\sigma^0 \mathbf{r}\cdot\mathbf{r} = |\Omega|^{-1}\int_{\Omega_m} |\nabla w+\mathbf{r}|^2\,dx, \quad \text{where } w \text{ is the } \Omega\text{-periodic solution of}$$

$$\mathbf{n}\cdot(\nabla w+\mathbf{r}) = 0 \quad \text{on } \Gamma_i,$$

$$\Delta w = 0 \quad \text{in } \Omega_m. \tag{6.7}$$

For any constant vector $\boldsymbol{\mu}$ the matrix G is defined by

$$\mathrm{G}\boldsymbol{\mu}\cdot\boldsymbol{\mu} = |\Omega|^{-1}\int_{\Omega} (\chi_m\boldsymbol{\mu})\cdot\Lambda(\chi_m\boldsymbol{\mu})\,dx, \tag{6.8}$$

where Λ is the projection of $L^2(\Omega)^3_{per}$ onto the space of gradients of periodic potentials in $H^1(\Omega)$. The tensor G appears in the anisotropic Hashin–Shtrikman bounds on the effective conductivity for the perfectly bonded case: see Willis (1982) and Kohn and Milton (1988). This tensor contains two-point correlation information on the pore microstructure. Indeed, G can be written as

$$\mathrm{G}_{il} = \sum_{k\neq 0}\frac{k_i k_l}{|\mathbf{k}|^2}|\Omega|^{-1}\int_{\Omega} e^{2\pi i\mathbf{k}\cdot\mathbf{t}} c_{bb}(\mathbf{t})\,dt,$$

where $c_{bb}(\mathbf{t})$ is the two-point correlation,

$$c_{bb}(\mathbf{t}) = |\Omega|^{-1}\int_{\Omega}\chi_p(\mathbf{x}+\mathbf{t})\chi_p(\mathbf{x})\,dx.$$

This function gives the probability that the ends of a rod of length and orientation described by the vector $\mathbf{t}$ lies in the pore phase. This description of G was given in Willis (1982).

Proof of Theorem 6.1. Equation (6.3) follows directly from substitution of the trial fields into the first two terms of (3.31). The term containing the matrix U in (6.4) also follows directly from substitution of trial fields in the variational principle. The terms involving the matrices $[\alpha_C/(-\alpha_T)QD](\sigma_m\mathrm{I}-\sigma^0)$ and G in (6.4) follow from expansion of the following nonlocal terms

$$\left(\overset{*}{D}\int_{\Omega_m}|K(\mathbf{v})|^2\,dx+\sigma_p\int_{\Omega}|N(\mathbf{p})+\alpha_T S(\mathbf{v})|^2\,dx\right)$$

in (3.31). We first establish the identity

$$\sigma_p|\Omega|^{-1}\int_{\Omega}|N(\mathbf{p})+\alpha_T S(\mathbf{v})|^2\,dx = \sigma_p^{-1}(\mathrm{G}((\alpha_T)\mathbf{r}-\boldsymbol{\mu})\cdot((\alpha_T)\mathbf{r}-\boldsymbol{\mu})). \tag{6.9}$$

To see this we substitute $\mathbf{p} = \chi_m\boldsymbol{\mu}$ into (3.26) to get

$$N(\chi_m\boldsymbol{\mu}) = -\frac{1}{\sigma_p}\sum_{\mathbf{k}\neq 0} e^{\frac{2\pi i\mathbf{k}\cdot\mathbf{x}}{L}}\frac{\mathbf{k}}{|\mathbf{k}|^2}(\mathbf{k}\cdot\hat{\chi}_m(\mathbf{k})\boldsymbol{\mu}). \tag{6.10}$$

To evaluate $S(\mathbf{v})$ we recall the definition of the operator T given by (3.28) to obtain

$$\int_\Gamma e^{-\frac{2\pi i\mathbf{k}\cdot\mathbf{y}}{L}} T\mathbf{v}\,ds = \sum_i \int_{\Gamma_i} e^{-\frac{2\pi i\mathbf{k}\cdot\mathbf{y}}{L}} T(\nabla_s \phi^j r_j)\,ds$$

$$= -\sum_i \int_{\Gamma_i} e^{-\frac{2\pi i\mathbf{k}\cdot\mathbf{y}}{L}} \mathbf{r}\cdot\mathbf{n}\,ds$$

$$= 2\pi i \mathbf{r}\cdot\mathbf{k}\hat{\chi}_p(\mathbf{k}). \tag{6.11}$$

Noting that for $\mathbf{k} \neq 0$, $\hat{\chi}_p = -\hat{\chi}_m$, we find that

$$S(\mathbf{v}) = \frac{1}{\sigma_p} \sum_{\mathbf{k}\neq 0} e^{\frac{2\pi i\mathbf{k}\cdot\mathbf{x}}{L}} \frac{\mathbf{k}}{|\mathbf{k}|^2} (\mathbf{k}\cdot\mathbf{r})\hat{\chi}_m(\mathbf{k}). \tag{6.12}$$

Identity (6.9) follows, observing that for any vector field $\mathbf{p}$ in $L^2(\Omega)^3_{per}$ the projection Λ is given by

$$\Lambda\mathbf{p} = \sum_{\mathbf{k}\neq 0} e^{\frac{2\pi i\mathbf{k}\cdot\mathbf{x}}{L}} \frac{\mathbf{k}}{|\mathbf{k}|^2} (\mathbf{k}\cdot\hat{\mathbf{p}}(\mathbf{k})) \tag{6.13}$$

and application of the Parceval identity.

Next we solve the auxiliary problem (3.22) and (3.23) for the choice $\mathbf{v} = \nabla_s \phi^j r_j$. We find that $C^{\mathbf{v}}$ is the solution of

$$-\frac{\alpha_C QD}{(-\alpha_T)} \nabla C^{\mathbf{v}}\cdot\mathbf{n} = \alpha_C T\mathbf{v} = \alpha_C(\nabla_s\cdot(\nabla_s\phi^j r_j)) = -\alpha_C \mathbf{r}\cdot\mathbf{n} \quad \text{on } \Gamma_i, \tag{6.14}$$

and

$$\Delta C^{\mathbf{v}} = 0 \quad \text{in } \Omega_m.$$

A straightforward calculation shows that

$$\overset{*}{D}|\Omega|^{-1} \int_{\Omega_m} |K(\mathbf{v})|^2\,dx = \frac{(-\alpha_T)\alpha_C}{QD} (\theta_m \mathrm{I} - \sigma^0)\mathbf{r}\cdot\mathbf{r}, \tag{6.15}$$

and the theorem follows.

Carrying out the optimization implied by (6.2) gives the lower bound on the effective conductivity tensor for anisotropic porous ceramics.

Theorem 6.2.

For any prescribed constant temperature gradient $\mathbf{E}$ in R^3

$$\sigma^e\mathbf{E}\cdot\mathbf{E} \geqslant \sigma_p\mathbf{E}\cdot\mathbf{E} + \begin{pmatrix} (\sigma_m-\sigma_p)^{-1}\theta_m\mathrm{I} + \sigma_p^{-1}\mathrm{G} & -\sigma_p^{-1}\mathrm{G} \\ -\sigma_p^{-1}\mathrm{G} & \sigma_p^{-1}\mathrm{G}+\mathrm{L} \end{pmatrix}^{-1} \begin{pmatrix} \sigma_m\mathbf{E} \\ \theta_p\mathbf{E} \end{pmatrix} \cdot \begin{pmatrix} \theta_m\mathbf{E} \\ \theta_p\mathbf{E} \end{pmatrix}. \tag{6.16}$$

The tensor of interfacial parameters given by (6.6) can be calculated explicitly for polydisperse suspensions of spherical pores. For suspensions of pores of arbitrary

shape this observation is generalized and the tensor is estimated in terms of the surface to volume dissipation associated with each pore. The surface to volume dissipation was introduced to describe size effects for composites with highly conducting interface in Lipton (1998). For a pore of unit thermal conductivity occupying the region B_i, its surface to volume dissipation 'β_i' is given by

$$\beta_i = \min_{\Delta u = 0, \text{in } B_i} \frac{\int_{\Gamma_i} |\nabla_s u|^2 \, \mathrm{d}s}{\int_{B_i} |\nabla u|^2 \, \mathrm{d}x}. \tag{6.17}$$

For a spherical pore with radius a, the surface to volume dissipation is $(2/a)$. Estimates for surface to volume dissipation in terms of the dimensions of the pores are given for convex and star-like pore shapes in Lipton (1998).

We make the following two observations:

Theorem 6.3.

For a suspension of spherical pores having different radii $a_1, \ldots, a_N$

$$\mathrm{U} = \theta_\mathrm{p} \frac{\langle a \rangle}{2} \mathrm{I}, \tag{6.18}$$

where $\langle a \rangle$ is the average pore radius for a given pore size distribution function as defined in (1.8).

For a suspension of arbitrarily shaped pores having different values of surface to volume dissipation $\beta_1, \ldots, \beta_N$, we define the quantity $\langle \beta^{-1} \rangle$ by

$$\langle \beta^{-1} \rangle = \theta_\mathrm{p} \sum_{i=1}^{N} \beta_i^{-1} D(\beta_i), \tag{6.19}$$

where $D(\beta_i)$ is the relative volume fraction of pores with surface to volume dissipation equal to β_i and $\Sigma_{i=1}^{N} D(\beta_i) = \theta_\mathrm{p}$.

Theorem 6.4.

For a suspension of pores having different values of surface to volume dissipation $\beta_1, \ldots, \beta_N$

$$\mathrm{U} \leqslant \theta_\mathrm{p} \langle \beta^{-1} \rangle \mathrm{I}. \tag{6.20}$$

Moreover, when the pores are spherical with radii $a_1, \ldots, a_N$, we have $\beta_i = (2/a_i)$ and (6.20) holds with equality.

To prove Theorems 6.3 and 6.4 we use the linearity of the boundary value problem (6.1) and write $\phi^{\mathbf{r}} = \phi^j r_j$ where

$$\Delta_s \phi^{\mathbf{r}} = -\mathbf{n} \cdot \mathbf{r} \quad \text{on } \Gamma_i \tag{6.21}$$

and

$$\Delta\phi^{\mathbf{r}} = 0 \quad \text{in the pore } B_i.$$

For a spherical particle of radius a is it shown in Lipton (1998) that the surface to volume dissipation is precisely $2/a$. The minimizer of (6.17) is the solution of (6.21) given by $\tilde{\phi}^{\mathbf{r}} = (a/2)\mathbf{r}\cdot(\mathbf{x}-\mathbf{x}^i)$ where $\mathbf{x}^i$ are the coordinates of the sphere center. Theorem 6.3 follows from the definition of U. To estimate U we write

$$\mathrm{U}\mathbf{r}\cdot\mathbf{r} = |\Omega|^{-1}\sum_{i=1}\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s, \tag{6.22}$$

and for each pore we estimate

$$\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s. \tag{6.23}$$

Integration by parts on the pore–matrix interface gives

$$\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s = -\int_{\Gamma_i}(\phi^{\mathbf{r}}\Delta_s\phi^{\mathbf{r}})\,\mathrm{d}s = \int_{\Gamma_i}\phi^{\mathbf{r}}(\mathbf{r}\cdot\mathbf{n})\,\mathrm{d}s. \tag{6.24}$$

Application of the Gauss–Green theorem, noting that $\Delta\phi^{\mathbf{r}} = 0$, gives

$$\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s = \int_{\Gamma_i}\phi^{\mathbf{r}}(\mathbf{r}\cdot\mathbf{n})\,\mathrm{d}s = \int_{B_i}\nabla\phi^{\mathbf{r}}\cdot\mathbf{r}\,\mathrm{d}x. \tag{6.25}$$

From Cauchy's inequality we have

$$\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s = \int_{B_i}\nabla\phi^{\mathbf{r}}\cdot\mathbf{r}\,\mathrm{d}x \leqslant \|\nabla\phi^{\mathbf{r}}\|_{L^2(B_i)}|B_i|^{1/2}|\mathbf{r}|. \tag{6.26}$$

From the definition of β_i it is evident that

$$\|\nabla\phi^{\mathbf{r}}\|^2_{L^2(B_i)} \leqslant \beta_i^{-1}\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s. \tag{6.27}$$

Application of (6.27) to (6.26) delivers the estimate

$$\int_{\Gamma_i}|\nabla_s\phi^{\mathbf{r}}|^2\,\mathrm{d}s = \leqslant \beta_i^{-1}|B_i|\,|\mathbf{r}|^2. \tag{6.28}$$

From the estimate and (6.22) it follows that

$$\mathrm{U}\mathbf{r}\cdot\mathbf{r} \leqslant |\Omega|^{-1}\left(|\Omega_{\mathrm{p}}|\sum_{i=1}\beta_i^{-1}\frac{|B_i|}{|\Omega_{\mathrm{p}}|}\right)|\mathbf{r}|^2, \tag{6.29}$$

where the region Ω_{p} is the union of all pore regions and Theorem 6.4 follows.

We apply the estimate for U given by Theorem 6.4 to (6.2) and obtain the following lower bound on the effective conductivity tensor for anisotropic suspensions of pores.

Theorem 6.5.

For any prescribed constant temperature gradient $\mathbf{E}$ in R^3

$$\sigma^e\mathbf{E}\cdot\mathbf{E} \geqslant \sigma_p\mathbf{E}\cdot\mathbf{E}+\begin{pmatrix}\tilde{\mathrm{A}} & \tilde{\mathrm{B}}\\ \tilde{\mathrm{B}} & \tilde{\mathrm{C}}\end{pmatrix}^{-1}\begin{pmatrix}\sigma_m\mathbf{E}\\ \theta_p\mathbf{E}\end{pmatrix}\cdot\begin{pmatrix}\theta_m\mathbf{E}\\ \theta_p\mathbf{E}\end{pmatrix}, \tag{6.30}$$

where

$$\begin{aligned}\tilde{\mathrm{A}} &= (\sigma_m-\sigma_p)^{-1}\theta_m\mathrm{I}+\sigma_p^{-1}\mathrm{G},\\ \tilde{\mathrm{B}} &= -\sigma_p^{-1}\mathrm{G},\\ \tilde{\mathrm{C}} &= \sigma_p^{-1}\mathrm{G}+\frac{\theta_p\langle\beta^{-1}\rangle}{Q\alpha_s(-\alpha_T)}\mathrm{I}+\frac{\alpha_C}{(-\alpha_T)QD}(\sigma_m\mathrm{I}-\sigma^0).\end{aligned} \tag{6.31}$$

We introduce the function

$$LB(z)\overset{\text{def}}{=}\sigma_p+\frac{(1-\theta_p)z+\dfrac{\theta_p^2}{\sigma_m-\sigma_p}+\dfrac{\theta_p}{3\sigma_p}}{\left(\dfrac{\theta_p}{3\sigma_p}+\dfrac{1}{\sigma_m-\sigma_p}\right)z+\dfrac{\theta_p(1-\theta_p)}{3\sigma_p(\sigma_m-\sigma_p)}}, \tag{6.32}$$

defined for $z\geqslant 0$. The function LB is decreasing with z. We introduce the dimensionless constants:

$$\tilde{A}_T=\frac{(-\alpha_T)\alpha_sQ}{\sigma_m-\sigma_p}\frac{1}{2\langle\beta^{-1}\rangle},\quad \tilde{A}_C=\frac{\alpha_C\alpha_s}{D}\frac{1}{2\langle\beta^{-1}\rangle}\left(\frac{1-\sigma^0}{\theta_p}-1\right), \tag{6.33}$$

and the variable t defined by

$$t=\theta_p(\sigma_m-\sigma_p)^{-1}\left(\frac{1+2\tilde{A}_C}{2\tilde{A}_T}\right). \tag{6.34}$$

The lower bound for statistically isotropic porous ceramics is given by:

Theorem 6.6. Lower bound on the effective conductivity tensor for statistically isotropic porous ceramics.

$$\sigma^e \geqslant LB(t). \tag{6.35}$$

For isotropic polydisperse suspensions of spheres $\langle\beta^{-1}\rangle=\langle a\rangle/2$ and Theorem 1.2 of Section 1 follows immediately.

We observe that $LB[\theta_p/(\sigma_m-\sigma_p)]=\sigma_m$ and from monotonicity we obtain the following:

Theorem 6.7. Lower energy dissipation inequality for isotropic suspensions of pores.

For any value of the pore volume fraction θ_p

If

$$\frac{2\tilde{A}_T}{1+2\tilde{A}_C} \geqslant 1, \tag{6.36}$$

then

$$\sigma^e \geqslant \sigma_m.$$

The monotonicity of the lower bound shows that for $t < \infty$,

$$\sigma^e \geqslant LB(t) > LB(\infty) = HS_-. \tag{6.37}$$

Here HS_- is the Hashin and Shtrikman (1962) lower bound for isotropic perfectly bonded two-phase composites.

It is evident from (6.34) that the parameter t is increasing as the value of σ^0 decreases. It follows that any lower bound on σ^0 delivers a lower bound on the effective conductivity σ^e. We consider suspensions of spherical pores of different radius for a given value of the geometric parameter 'q'. For this case one has the lower bound on σ^0 derived by Bruno (1991)

$$\sigma^0 \geqslant W(0) = \frac{1-S_M}{1-S_m}\left(1+\frac{\left(1-\dfrac{\theta_p}{\delta}\right)^2}{(1-\theta_p/\delta)((1-S_M)/\delta)+(\theta_p/\delta^2)((\theta_m/3)-S_m)}\right). \tag{6.38}$$

Here, $\delta = S_M - S_m$, where $S_m = (1/3)(1-q^3)$ and $S_M = A/(1+A)$. Here, A depends upon q and is computed numerically. Estimating σ^0 using (6.38) delivers a lower bound in terms of pore volume fraction, average pore size $\langle a\rangle$ and 'q'. The bound is given by:

Theorem 6.8. Lower bound for the effective conductivity of a polydisperse suspension of spherical pores with statistically specified pore microstructure.

$$\sigma^e \geqslant LB(t(W(0)))$$

where

$$t(W(0)) = \frac{\theta_p\langle a\rangle}{2\alpha_s(-\alpha_T)Q}\left(1+\frac{2(\alpha_s)\alpha_s}{\langle a\rangle D}\left(\frac{1-W(0)}{\theta_p}-1\right)-\frac{2\alpha_s(-\alpha_T)Q}{\langle a\rangle(\sigma_m-\sigma_p)}\right) + \frac{\theta_p}{\sigma_m-\sigma_p}, \tag{6.39}$$

and the lower bound function LB is given by (6.32).

For monodisperse suspensions of spherical pores of radius a with prescribed nearest neighbor distribution function $H(x)$, the lower bound on σ^0 is given by the security sphere bound developed by Torquato and Rubinstein (1991)

$$\sigma^0 \geqslant F(H) = \frac{1}{1+2a\theta_p \int_1^\infty \frac{3x^3}{2(x^3-1)} H(x)\,dx}. \tag{6.40}$$

Estimation of σ^0 using (6.40) delivers a lower bound in terms of pore volume fraction, pore size a and nearest neighbor distribution function '$H(x)$' given by:

Theorem 6.9. *Lower bound for the effective conductivity of a monodisperse suspension of spherical pores with statistically specified pore microstructure.*

$$\sigma^e \geqslant LB(t(F(H))),$$

where

$$t(F(H)) = \frac{\theta_p a}{2\alpha_s(-\alpha_T)Q}\left(1+\frac{2(\alpha_s)\alpha_C}{aD}\left(\frac{1-F(H)}{\theta_p}-1\right)-\frac{2\alpha_s(-\alpha_T)Q}{a(\sigma_m-\sigma_p)}\right) + \frac{\theta_p}{\sigma_m-\sigma_p}. \tag{6.41}$$

7. Physical interpretation of the parameters A_T, $\tilde{A}_T$, A_C and $\tilde{A}_C$ and bounds on the effective conductivity for a model of Y_2O_3

In this section we provide the physical interpretation for the parameters A_T, $\tilde{A}_T$, A_C and $\tilde{A}_C$ and discuss their relation to the parameters K_T and K_C introduced in Gambaryan et al. (1993). We provide plots of the upper and lower bounds on the effective conductivity for a yttrium oxide ceramic as functions of the pore radius.

We introduce the parameters K_T and K_C given by Gambaryan et al. (1993) for monodisperse suspensions of spherical pores of radius a

$$K_T = \frac{(-\alpha_T)\alpha_s Q}{\sigma_m} a^{-1}, \quad K_C = \frac{\alpha_C\alpha_s}{D} a^{-1}, \tag{7.1}$$

and recall the parameters A_T, A_C, $\tilde{A}_T$ and $\tilde{A}_C$ given by eqns (1.10) and (1.13). To relate the two sets of parameters, we neglect the effects of the surrounding pores and consider a single pore of radius a embedded in an infinite matrix. Mathematically this is expressed by representing the effective conductivities σ^∞ and σ^0 by their dilute expansions

$$\sigma^\infty = 1+3\theta_p+O(\theta_p^2) \quad \text{and} \quad \sigma^0 = 1-\tfrac{3}{2}\theta_p+O(\theta_p^2). \tag{7.2}$$

For a single pore, $\langle a\rangle = a$, $\langle a^{-1}\rangle = a^{-1}$ and

$$A_{\mathrm{C}} = \frac{K_{\mathrm{C}}}{2} + O(\theta_{\mathrm{p}}), \quad \tilde{A}_{\mathrm{C}} = \frac{K_{\mathrm{C}}}{2} + O(\theta_{\mathrm{p}}). \tag{7.3}$$

Neglecting higher-order terms we have:

$$A_{\mathrm{C}} = \tilde{A}_{\mathrm{C}} = \frac{K_{\mathrm{C}}}{2}. \tag{7.4}$$

One also has:

$$A_{\mathrm{T}} = \tilde{A}_{\mathrm{T}} = \frac{(-\alpha_{\mathrm{T}})\alpha_{\mathrm{s}} Q}{a(\sigma_{\mathrm{m}} - \sigma_{\mathrm{p}})}. \tag{7.5}$$

It is clear that $A_{\mathrm{T}} = K_{\mathrm{T}}$ for dilute suspensions of nonconducting pores. Arguing as in Gambaryan et al. (1993), we suppose that a characteristic temperature drop ΔT across a single pore of radius a results in the corresponding changes ΔC and ΔC_{s}. We note that the combination α_{s}/a has dimensions of diffusivity and applying the definitions of the coefficients α_{T} and α_{C} gives the following:

$$A_{\mathrm{C}} = \tilde{A}_{\mathrm{C}} = \frac{1}{2}\frac{(\alpha_{\mathrm{s}}/a)\Delta C_{\mathrm{s}}}{a}\frac{a}{D\Delta C} = \frac{1}{2}\frac{q_{\mathrm{s}}}{q}, \tag{7.6}$$

$$A_{\mathrm{T}} = \tilde{A}_{\mathrm{T}} = \frac{(-\alpha_{\mathrm{s}}/a)\Delta C_{\mathrm{s}} Q}{a}\frac{1}{\dfrac{\sigma_{\mathrm{m}}\Delta T}{a} - \dfrac{\sigma_{\mathrm{p}}\Delta T}{a}} = \frac{-q_{\mathrm{s}} Q}{j_{\mathrm{m}} - j_{\mathrm{p}}}, \tag{7.7}$$

where j_{p} is the convective heat flux across the pore filled with the pore gas, j_m is the convective heat flux across the pore if it were replaced with matrix material, q_{s} is the concentration flux of impurities on the surface and q is the concentration flux of impurities in the neighborhood surrounding the pore. The quantity $-q_{\mathrm{s}}Q$ is the net heat flux across the pore due to the segregation–diffusion process. Thus, in the dilute limit, the parameters A_{T} and $\tilde{A}_{\mathrm{T}}$ characterize the relative enhancement of the heat flux across a pore due to the segregation–diffusion process, while A_{C} and $\tilde{A}_{\mathrm{C}}$ are measures of the mass transfer of impurities from the matrix to the pore surface relative to the flux of impurities in the neighborhood surrounding the pore. These interpretations can be extrapolated to the non-dilute setting, noting that the factors $\{[(\sigma^{\infty}-1)/\theta_{\mathrm{p}}]-1\}^{-1}$, $\{[(1-\sigma^{0})/\theta_{\mathrm{p}}]-1\}$ and averages $\langle a\rangle$, $\langle a^{-1}\rangle$ appearing in the formulas for A_{T}, A_{C}, $\tilde{A}_{\mathrm{T}}$ and $\tilde{A}_{\mathrm{C}}$ are corrections taking into account the presence of other particles. The approach of Gambaryan et al. (1993) follows Maxwell's (1892) treatment, therefore, the parameters K_{T} and K_{C} naturally do not take into account the presence of neighboring spheres.

The upper and lower bounds given by (5.21) and (6.41) are used to estimate the effective conductivity of a random, monodisperse suspension of pores. The material properties of the suspension are chosen to represent a yttrium oxide ceramic. We suppose the porosity is high, $\theta_{\mathrm{p}} = 0.4$ and that the minimum distance between neighboring pores is 0.1% of the pore radius. For this case the parameters $J(H)$ and $F(H)$ are given by $J(H) = 43.67$ and $F(H) = 0.45$. When the temperature is greater than 1000°C almost all the segregated substance is dissolved in the bulk phase (see Gam-

baryan et al., 1993), and we set $\alpha_C = 0$. It is evident from Theorem 1.4 that the upper and lower bounds coincide when the pore radius equals the critical value R given by $R = [2Q\alpha_s(-\alpha_T)/(\sigma_m - \sigma_p)]$. This effect is illustrated in Fig. 1 for the normalized effective thermal conductivity σ^e/σ_m at 1200°C. Here we have taken $Q = 75$ KJ/mol, $\alpha_s = 6 \times 10^{-10}$ ms^{-1}, $\sigma_m = 3$ W/mK and $\sigma_p = 10^{-6}$ W/mK. The value of the parameter α_T at 1200°C, is estimated from Fig. 4 of Gambaryan et al. (1993). The same bounds are plotted for pore radii up to one micrometer in Fig. 4. In Table 1 we provide values of the critical radius for temperatures between 1000–1300°C.

To illustrate the effect of the parameter α_C we keep all other parameters the same and plot the bounds on the normalized effective thermal conductivity σ^e/σ_m for finite values of $\alpha_C\alpha_s/D$ in Figs 2 and 3. It is seen from Figs 2 and 3 that the upper bound remains fixed for small values of α_C while the lower bound decreases significantly.

It should be noted that the conductivity and diffusivity parameters for the interface and matrix phase are estimated for the Y_2O_3 system, so the results in this section give

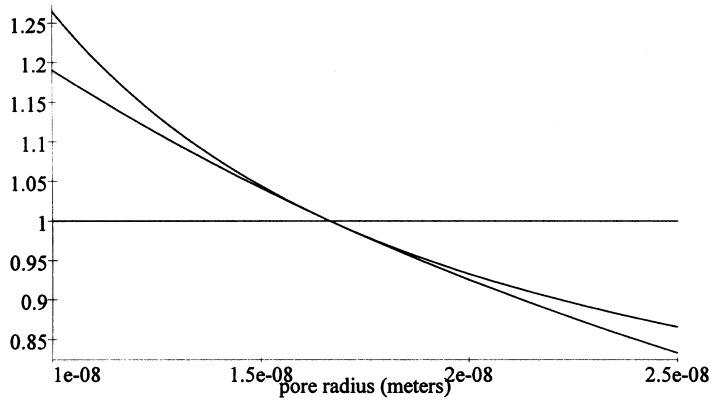

Fig. 1. Bounds on effective conductivity for $\alpha_C\alpha_s/D = 0$.

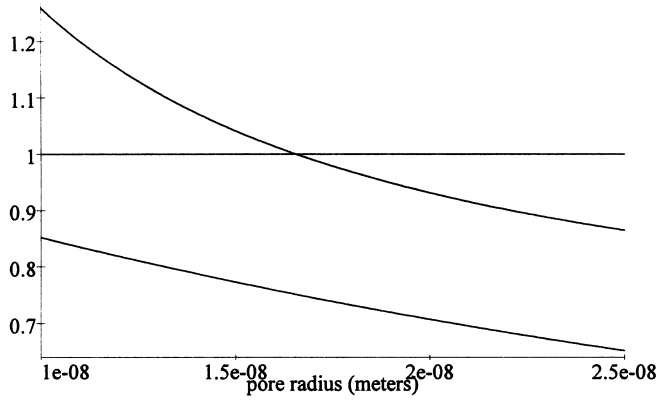

Fig. 2. Bounds on effective conductivity for $\alpha_C\alpha_s/D = 2 \times 10^{-8}$.

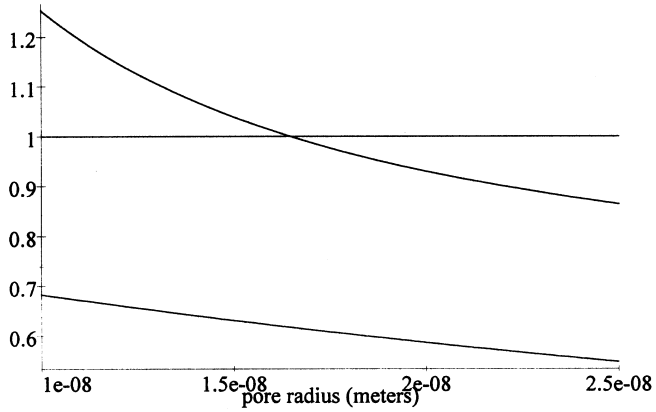

Fig. 3. Bounds on effective conductivity for $\alpha_C\alpha_s/D = 4 \times 10^{-8}$.

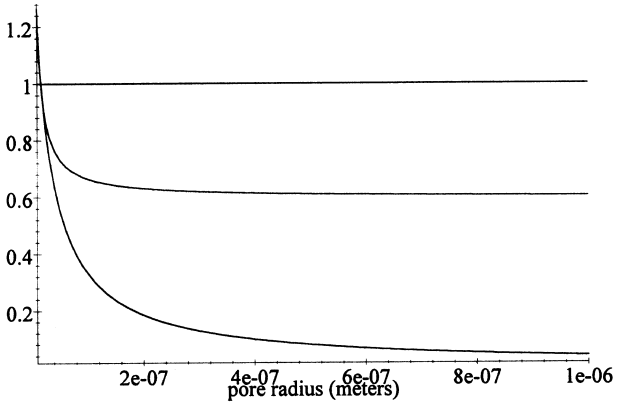

Fig. 4. Bounds on effective conductivity for $\alpha_C\alpha_s/D = 0$.

Table 1

R	Temperature (°C)
3.33×10^{-8} m	1300
1.66×10^{-8} m	1200
0.33×10^{-8} m	1000

only a qualitative description of the dependence of the effective conductivity on the pore size.

The methods used in this paper are variational in nature and allow one to treat the problem directly without approximating the field interactions between pores. The

results given in this work corroborate the behavior of the effective thermal conductivity on the parameters K_T and K_C as reported in Gambaryan et al. (1993). Moreover, the treatment given here predicts for the first time, new size effects, critical radii and energy dissipation inequalities for heat conduction in the presence of coupled heat and mass transport processes at the two phase interface.

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References

Bruno, O., 1991. The effective conductivity of strongly heterogeneous composites. Proc. R. Soc. Lond. A 433, 353–381.

Chandrasekhar, S., 1965. The stability of a rotating drop. Proc. R. Soc. Lond. A 286, 1–26.

Gambaryan, T., Litovsky, E., Shapiro, M., 1993. Influence of segregation–diffusion processes on the effective thermal conductivity of porous ceramics. Int. J. Heat Mass Transfer 36, 4123–4131.

Hashin, Z., Shtrikman, S., 1962. A variational approach to the theory of the effective magnetic permeability of multiphase materials. J. Appl. Phys. 33, 3125–3131.

Kingrey, W.D., 1974. Plausible concepts necessary for sufficient interpretation of ceramic grain–boundary phenomena: II, solute segregation, grain boundary diffusion and general discussion. J. Amer. Ceram. Soc. 57, 74–83.

Kingrey, W.D., Bowen, H.K., Uhlman, D.R., 1976. Introduction to Ceramics. Wiley, New York.

Lipton, R., 1997. Variational methods bounds and size effects for composites with highly conducting interface. J. Mech. Phys. Solids 45, 361–384.

Lipton, R., 1998. Influence of interfacial surface conduction on the DC electrical conductivity of particle reinforced composites. Proc. R. Soc. Lond. A 454, 1371–1382.

Lipton, R., Vernescu, B., 1995. Variational methods, size effect bounds and extremal microgeometries for elastic composites with imperfect interface. Mathematical Models and Methods in Applied Science 5, 1139–1173.

Lipton, R., Vernescu, B., 1996. Composites with imperfect interface. Proc. R. Soc. Lond. A 452, 329–358.

Litovski, E. Ya., Klimovich, A.V., 1978. On contribution of segregation and diffusion processes to thermal conductivity of refractories. J. Engng Phys. 42, 908–911.

Maxwell, J.C., 1892. Treatise on Electricity and Magnetism, vol. I. Oxford University Press, London.

Milton, G.W., Kohn, R.V., 1988. Variational bounds on the effective moduli of anisotropic composites. J. Mech. Phys. Solids 36, 597–629.

Torquato, S., Rubinstein J., 1991. Improved bounds on the effective conductivity of high-contrast suspensions. J. Appl. Phys. 69, 7118–7125.
Torquato, S., Lu, B., Rubinstein, J., 1990. Nearest-neighbor distribution functions in many-body systems. Physical Review A 41, 2059–2075.
Willis, J.R., 1982. Elasticity theory of composites. In: Hopkins, H.G., Sewel, M.J. (Eds.), Mechanics of Solids. Pergamon Press, Oxford.